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FY 2009 PROGRESS REPORT FOR THE DOE HYDROGEN PROGRAM

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Approved by Sunita Satyapal, Acting Hydrogen Program Manager

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I. INTRODUCTION

I.0 Introduction

The DOE Hydrogen Program (the Program) has conducted comprehensive and focused efforts to enable the widespread commercialization of fuel cells in diverse sectors of the economy. With emphasis on applications that will most effectively strengthen our nation's energy security and improve our stewardship of the environment, the Program engages in research, development, and demonstration (RD&D) of critical improvements in the technologies, as well as diverse activities to overcome economic and institutional obstacles to commercialization. The Program addresses the full range of barriers facing the development and deployment of fuel cell technologies by integrating basic and applied research, technology development and demonstration, and other supporting activities. In addition to DOE's Office of Energy Efficiency and Renewable Energy (EERE), the Program includes the DOE Offices of Nuclear Energy, Fossil Energy, and Science.

In Fiscal Year 2009, Congress appropriated \$269 million for the DOE Hydrogen Program. The Program is organized into distinct sub-programs focusing on specific areas of research and development (R&D), as well as other activities to address non-technical challenges. The goals, objectives, and targets of each of the applied research programs are identified in the multi-year program plans for EERE, the Office of Fossil Energy, and the Office of Nuclear Energy; and the basic research areas addressed by the Office of Science are described in *Basic Research Needs for the Hydrogen Economy—Report of the Basic Energy Sciences Workshop on Hydrogen Production, Storage, and Use*. All of these documents are available at www.hydrogen.energy.gov/program_plans.html.

In the past year, the Program made substantial progress toward its goals and objectives. Highlights of the Program's accomplishments are summarized in the following.

PROGRAM PROGRESS AND ACCOMPLISHMENTS

Fuel Cells

The Fuel Cell Sub-Program has made significant advances in reducing the high-volume cost of fuel cell systems; improving membrane performance under hot, dry operating conditions; and characterizing fuel cell materials and components. In FY 2009, an independent review panel validated the Program's assessment that the high-volume cost of fuel cells was reduced by 23%, from \$94/kW in 2007 to \$73/kW in 2008. Moreover, the panel approved of DOE's cost analysis methodology and concluded that a range of \$60/kW to \$80/kW is a "valid estimation of the potential manufactured cost for an 80-kW_{net} fuel cell system, based on 2008 technology."¹ Based on further progress during the past year, primarily by reducing platinum (Pt) loading and improving power density, the FY 2009 cost assessment showed that the high-volume fuel cell system cost is \$61/kW, as indicated in Figure 1.

High catalyst cost associated with the use of Pt and other platinum group metals (PGMs) limit potential cost reductions. As a result, strong focus is given to reducing the loading of these metals in the stack, while maintaining performance. One example of progress is the development of innovative

FIGURE 1. DOE-funded R&D has resulted in significant cost reductions of fuel cells, achieving \$61/kW as the projected high-volume cost of an 80 kW_{net} automotive fuel cell system based on state-of-the-art technology in FY 2009.

¹ *Fuel Cell System Cost for Transportation—2008 Cost Estimate*, National Renewable Energy Laboratory, May 2009, <http://hydrogen.doedev.nrel.gov/pdfs/45457.pdf>.

PGM-based nanostructured catalysts by Brookhaven National Laboratory, achieving low Pt-loading and high activity. The performance of these catalysts compares favorably with that of the baseline Pt/C catalyst (Figure 2). In FY 2009, Los Alamos National Laboratory (LANL) developed two paths toward high-performance fuel cell cathodes that use no Pt or PGMs. Results showed a five-fold and an eleven-fold improvement over the best performing non-noble catalyst of the past year. In 2009, 3M continued to play a significant role in fuel cell system cost reduction, demonstrating a new baseline membrane electrode assembly (MEA) with a 40% decrease in loading from 2008. The 3M MEA exceeded—by more than 30%—DOE's lifetime targets for minimal surface area and performance loss under open-circuit voltage hold tests.

Major progress was also made this year in the development of high-temperature membranes capable of operating at low relative humidity (RH). Giner Electrochemical Systems demonstrated a perfluorosulfonic acid (PFSA) membrane with conductivity at least 2.5 times that of Nafion[®] under hot, relatively dry conditions, exceeding the DOE 2009 conductivity milestone of 0.1 S/cm at 120°C and 50% RH.

LANL researchers examined the effects of impurities on fuel cell performance and durability, finding that sub-ppm levels of H₂S in hydrogen fuel caused significant performance loss, with degradation occurring due to catalyst poisoning in both the anode and the cathode. The ability of a contaminant in the anode inlet to cause degradation of the cathode demonstrates the important role of contaminant crossover in performance degradation.

In FY 2009, the Fuel Cell Sub-Program expanded its focus—which had been primarily on longer-term transportation applications—to include more nearer-term applications of fuel cells including distributed power (primary and backup), portable power, auxiliary power units, material handling equipment, and specialty vehicles. Fuel cell technology already provides sufficient performance and durability to be competitive with alternative technologies in some of these applications, while in others, some improvements are still required.

Hydrogen Storage

In FY 2009, the Storage Sub-Program continued to make progress in all three classes of materials under investigation—hydrogen sorbents, reversible metal hydrides, and chemical hydrogen storage. These achievements involved improvements in operational properties, not just in storage capacity.

An initial down-select process by the Chemical Hydrogen Storage Center of Excellence (CoE) examined about 120 materials and combinations of materials, resulting in approximately 85% being discontinued, allowing resources to be focused on improving the kinetics and capacities for hydrogen release through the use of catalysts and other additives. A detailed cost estimate for the regeneration of one of the key materials studied, ammonia borane (AB), indicated a cost of \$7–8/kg H₂ for large-scale production. Costs were found to be driven by capital equipment recovery costs and the cost of utilities. Development of an approach using hydrazine to form the BH₃-containing species may regenerate decomposed AB in just one or two steps, reaching thermodynamic efficiencies of 83%.

FIGURE 2. The Program is developing innovative nanostructured catalysts as a means of improving fuel cell performance while reducing cost. Pd-interlayer core/shell nanoparticles developed at Brookhaven National Laboratory have electrocatalytic activity superior to that of conventional Pt/C catalysts, but use less than 1/3 of the platinum.²

² P. Zelenay, "Advanced Cathode Catalysts," 2009 Annual Merit Review Proceedings, DOE Hydrogen Program, 2009, www.hydrogen.energy.gov/pdfs/review09/fc_21_zelenay.pdf.

Progress continued on increasing the hydrogen release rates from several ionic liquid/AB mixtures at temperatures below 120°C along with a total release that exceeded 10 wt%.

The Metal Hydride CoE continued a materials down-select process, with down-select decisions based on material reversible capacity, sorption thermodynamics, and kinetics. One achievement in this area was the electrochemical synthesis of high yields of pure alane (AlH_3) that avoids expensive thermodynamic routes for its reversible regeneration, making the hydride a more viable storage candidate. The University of Hawaii, along with HRL Laboratories, developed a low-temperature homogenous organometallic approach to incorporate about five times higher amounts of MgH_2 into carbon aerogels than was achieved via molten Mg metal. Additionally, in FY 2009 the aluminoborane compound, $\text{AlB}_4\text{H}_{11}$, was found to start releasing hydrogen at 125°C and desorb 10.5 wt% H_2 by heating to 325°C, suggesting that this material and related species may be good candidates for on-board hydrogen storage.

The Hydrogen Sorption CoE completed a down-select process that resulted in one third of the materials being continued. Research efforts from Rice University, Air Products, and the National Renewable Energy Laboratory were devoted to gaining a better understanding of the mechanisms for the hydrogen spillover effects of metal particles on sorbent surfaces to improve both kinetics and storage capacity. Caltech explored layered carbon structures as a means to increase the hydrogen sorption enthalpy and demonstrated an increase from the nominal range of 4–6 kJ/mole to 8.5–13 kJ/mole, thus retaining 50% of the liquid nitrogen temperature capacity at 195 K.

In addition to the advancements made by the CoEs, the Storage Sub-Program furthered technology in the areas of compressed and cryogenic tanks and materials properties and testing. Composite tank systems with 350-bar and 700-bar compressed gas storage were analyzed, and the tank designs were revised accordingly. Lawrence Livermore National Laboratory designed and fabricated a cryogenic vessel for cryo-compressed hydrogen storage with promising cost results compared to conventional liquid hydrogen. As part of an international cooperative program, research groups in Canada, Germany, and Japan (along with U.S. partners) are assessing the chemical reactivity and safety aspects of representative hydrogen storage materials. The U.S. partners' activities in this cooperative effort included Savannah River National Laboratory developing models assessing potential release scenarios, Sandia National Laboratories investigating risk mitigation strategies, and United Technologies Research Center (UTRC) performing failure mode effects analysis.

In FY 2009, working in conjunction with the Hydrogen Storage Technical Team, the Storage Sub-Program released revised performance targets for on-board storage systems, consistent with the

FIGURE 3. In FY 2009, storage targets were revised and the three Storage Centers of Excellence continued to make progress in the down-selection of materials.

multi-year plans developed in 2003 which called for a reassessment of targets as more real-world data became available (Figure 3). When revising the targets, two key assumptions were maintained: targets are to be based on the application requirements, not the projected capabilities of storage technologies; and targets must allow for sufficient fuel storage for a driving range greater than 300 miles, without compromising passenger/cargo space or vehicle performance for the majority of light-duty vehicles. A key new assumption was that there would be differences in vehicle architecture between fuel cell and gasoline internal combustion engine (ICE) vehicles. In addition, real-world fuel cell vehicle fleet data were considered when establishing assumptions for fuel requirements, fuel economy, and weight and volume constraints; instead of the expected improvements over gasoline ICE vehicles that had been assumed earlier. Revised cost targets will be released in the future. The complete revised hydrogen storage performance targets can be found at: www1.eere.energy.gov/hydrogenandfuelcells/storage/pdfs/targets_onboard_hydro_storage.pdf.

Hydrogen Production

Renewable-Based Hydrogen. Advances in biofuel-reforming technology continued to reduce the cost of bio-derived hydrogen. Pacific Northwest National Laboratory demonstrated a significant increase in hydrogen yields by optimizing catalyst formulations and reaction conditions for vapor phase reforming at low pressure. Researchers at UTRC announced greater than 95% conversion of cellulosic biomass with 74% hydrogen selectivity. These high-yield processes bring hydrogen from biomass and bio-derived liquids closer to the 2014 cost targets of \$3.30/gasoline gallon equivalent (gge) and \$3.80/gge, respectively.

Technoeconomic analyses were performed on solar hydrogen production pathways. One study that was completed focused on several high-temperature thermochemical cycles, which resulted in the down-selection of the ZnO cycle and the identification of critical tasks for the remaining cycles, allowing resources to be applied effectively. In another study, Directed Technologies, Inc. (DTI) examined the photoelectrochemical direct water splitting pathway. With costs ranging from \$4 to \$10/gge for this approach, the analysis identified several viable pathways to meet the production cost targets. DTI also completed a separate boundary level technoeconomic analysis for hydrogen production costs from four different biological processes, again finding several production pathways that can meet long-term hydrogen production cost targets.

Significant increases were achieved in the productivity of photosynthetic organisms (microalgae and plants), with direct benefits for employing photosynthesis for hydrogen, biodiesel, or biomass production. Researchers at the University of California, Berkeley, achieved 15% solar energy conversion efficiency in a photosynthetic organism, a substantial improvement over the 3% efficiency measured in naturally existing organisms. This effort entails application of biotechnology approaches to reduce the size of (or “truncate”) light-harvesting chlorophyll antennae. Truncated chlorophyll antennae reduce shading of cells deeper in the mass culture, resulting in greater sunlight utilization efficiency and improved photosynthetic productivity. Genes identified in this work can be applied to other photosynthetic organisms and can benefit the production of biofuels in addition to hydrogen.

Another pathway for renewable-based hydrogen is electrolysis using power from renewable energy sources. Giner Electrochemical Systems demonstrated 1,000-hour single-cell membrane activity, and from this research, they projected an electrolyzer membrane lifetime of 45,000 to 55,000 hours (Figure 4). Researchers at Giner are also testing a new biphenyl sulfone membrane that is less than half the cost of their current membranes. Under nominal operating conditions, these membranes show 75% efficiency (lower heating value) for a single cell. Long-term durability tests are planned.

Hydrogen from Coal. Progress was made toward 2010 hydrogen separation targets, with Eltron Research, Inc. and Southwest Research Institute® demonstrating membranes in bench-scale tests, that have the ability to meet all of the Office of Fossil Energy’s targets. The Eltron membrane cost estimates would make it competitive with conventional technology. Southwest Research Institute® has produced a self-supported Pd-Cu alloy membrane with a thickness (5 microns) that is 1/5 of the 2007 state-of-the-art. This demonstrated progress was echoed by preliminary economic analysis that shows membranes have the potential for lower electricity cost, higher thermal efficiency, and improved CO₂ capture compared to conventional technologies.

FIGURE 4. Giner Electrochemical Systems PFSA membrane demonstrating 1,000-hour single membrane activity.

Nuclear Hydrogen. In FY 2009 Idaho National Laboratory operated their integrated laboratory-scale high temperature electrolysis unit for 45 days. This demonstration achieved a peak output of 5,650 liters per hour at 12-kWe input. Savannah River National Laboratory (SRNL) developed new operating methods that demonstrated electrolyzer operation without limitations caused by sulfur build-up.

Hydrogen Delivery

Researchers continued to make major advances in modeling hydrogen delivery infrastructure through the Hydrogen Delivery Scenario Analysis Model (HDSAM), finding only a 15% increase in the gaseous hydrogen fueling costs of a high pressure cascade system at 700 bar versus 350 bar. Cryo-compressed fueling was also added to the model, and analysis using HDSAM showed that hydrogen station costs for cryo-compressed fueling, using a cryopump, were 70% lower than station costs for fueling 700-bar vehicles using booster compressors. A version of the Hydrogen Rail Components Model was developed as an add-on to HDSAM, with preliminary analysis suggesting rail delivery as a viable low-cost option for long-distance transport.

Researchers were also successful in making progress in a variety of delivery technologies, including fiber reinforced polymer (FRP) pipelines and gaseous tube trailers. SRNL concluded a testing regimen on FRP pipelines and found positive results for hydrogen compatibility and blow-down testing. Leakage rate tests measured a rate of 0.02%, exceeding the DOE 2017 target of less than 0.5%. Advances in tube-trailer technologies included the successful testing of manufacturing procedures for 600-kg hydrogen tanks and innovative tube-trailer designs using high-strength, low-cost glass fiber, with triple the capacity of conventional tube-trailers.

FIGURE 5. These modeled high-volume costs of hydrogen delivery assume current technology, with a potential 2030 market penetration of 25% and hydrogen delivered 62 miles from a production plant to Los Angeles.

In FY 2009, continued progress was made in the areas of compression and liquefaction, essential technologies for reducing hydrogen delivery costs. Significant cost savings for early markets could be attained through the use of mass-produced compressor components. Researchers at Concepts NREC are developing a centrifugal compressor for hydrogen made from off-the-shelf components designed for natural gas service. In liquefaction, Prometheus Energy is working on an innovation called the Active Magnetic Regenerative Liquefier, which utilizes magnetic cooling, and could reduce energy consumption by 50% and reduce the liquefaction capital costs by 30%. Prototype development began in 2009.

Systems Analysis

The Systems Analysis Sub-Program continued to focus on the development of core models for hydrogen analysis and on conducting resource, infrastructure, well-to-wheels (WTW), and hydrogen quality analysis for different hydrogen production and delivery pathways. Significant progress was made in FY 2009 in the areas of early market analysis, the development and updating of analysis models, and analysis of the environmental impacts of hydrogen.

For example, Oak Ridge National Laboratory performed a sensitivity analysis to examine the potential effects on fuel cell vehicle market penetration of not meeting the Program's on-board hydrogen storage targets. The analysis showed a reduction from 95% to 50% vehicle penetration rates by 2050 if storage costs were \$17/kWh versus the storage target of \$2/kWh. Another important cost factor is hydrogen quality. Argonne National Laboratory developed a model to analyze the impact of hydrogen quality on fuel cell performance and the hydrogen production costs associated with meeting the required hydrogen quality specifications—the results showed a cost increase of less than \$0.05/gge.

Industry, academia, and national laboratories peer-reviewed the H2A Stationary Power Model, which addresses combined heat and power generation for proton exchange membrane, phosphoric acid, and molten carbonate fuel cells. Features of the model include analysis of power, heat, and hydrogen fuel costs based on capital equipment costs, feedstock prices, operating climate conditions, as well as heat and power loads.

FIGURE 6. Tri-generation of electricity, heat, and hydrogen (also called CHHP – combined heat, hydrogen and power) can achieve market penetration in areas of high electric prices, moderate natural gas prices and emerging demand for hydrogen for transportation fuel.

Well-to-Wheels Greenhouse Gas Emissions

(life cycle emissions, based on a projected state of the technologies in 2020)

*Net emissions from these pathways will be lower if these figures are adjusted to include:

- The displacement of emissions from grid power-generation that *will* occur when surplus electricity is co-produced with cellulosic ethanol
- The displacement of emissions from grid power-generation that *may* occur if electricity is co-produced with hydrogen in the biomass and coal pathways, and if surplus wind power is generated in the wind-to-hydrogen pathway
- Carbon dioxide sequestration in the biomass-to-hydrogen process

FIGURE 7. (above) and **FIGURE 8** (below): WTW analysis shows the potential for reductions in greenhouse gas emissions and petroleum consumption through the use of a number of technologies DOE is developing, including fuel cell vehicles using hydrogen from several production pathways. These results are documented in Program Record #9002, www.hydrogen.energy.gov/program_records.html.

Well-to-Wheels Petroleum Energy Use

(based on a projected state of the technologies in 2020)

The Macro-System Model (MSM) links existing and emerging models to simulate the performance and evolution of hydrogen infrastructure. In FY 2009, the MSM was used in analysis to support decision-making and was updated to include HyDRA, the resources model; HyPro, the infrastructure model; and HDSAM, the updated delivery model. One of the existing models, GREET, used for WTW analysis, was modified to include conventional and alternative-fuel plug-in hybrid electric vehicles, through coordination across programs within DOE. These enhanced analysis capabilities increase the ability to accurately assess the entire portfolio of vehicles and ensure consistent, transparent and most up-to-date assumptions across technologies. Similarly, greenhouse gas emissions using various electrical sources such as the U.S. grid or the California grid can be compared using the WTW analysis.

Manufacturing R&D

The key goals of Manufacturing R&D are to reduce the cost of producing fuel cell systems and hydrogen technologies and to enable increases in manufacturing rates and capacities. A number of advances were achieved in FY 2009: UltraCell created a specification for leak-testing and analyzed fuel cell stack manufacturing methods; Ballard down-selected a tool to measure the weight of gas diffusion layer coatings, demonstrating a means of achieving six-sigma quality standards; and researchers at Rensselaer Polytechnic Institute (RPI) demonstrated a reduction in cycle time for joining electrodes to sub-gaskets, from one minute with thermal bonding to one second with ultrasonic welding (Figure 9).

FIGURE 9. RPI's work on ultrasonic welding for MEA pressing.

Basic Research

In FY 2009, the Office of Science, Basic Energy Sciences (BES) continued to make progress in basic research for hydrogen and fuel cell technologies, with projects continuing in hydrogen storage, nanoscale catalysts, membranes, hydrogen production, and bio-inspired hydrogen research. Researchers funded by BES have learned how to tune hydrogen binding to metal-organic framework materials with exposed transition metal sites by influencing their magnetic spin state, utilized their understanding of crystal growth to tailor the synthesis of highly efficient crystals for photo generation of hydrogen, and created a bio-hybrid catalyst for hydrogen production using self-assembled carbon nanotubes linked to [FeFe] hydrogenase. At the FY 2009 Annual Merit Review and Peer Evaluation Meeting, researchers funded by the Office of Basic Energy Sciences on the topic of hydrogen storage presented their work through 14 oral and 11 poster presentations to help further coordination between the applied and basic research communities. The Office of Science also announced 46 Energy Frontier Research Centers (EFRCs) with a planned commitment of \$777 million over five years. Some of the EFRC efforts are relevant to the mission of the Hydrogen Program, and further coordination is planned in FY 2010.

Tracking the Commercialization of Technologies

One indicator of the robustness and innovative vitality of a research and development program is the number of patents applied for and granted. Each year, the DOE Hydrogen Program tracks the number of patents that are filed by or awarded to projects it sponsors. In FY 2009, 11 new patents were issued for discoveries or technologies developed in DOE Hydrogen Program projects; 21 more applications were filed or are in the process of being awarded, based on information provided by researchers in their Annual Progress Reports (Figure 10). In addition, the Program commissioned a

study of EERE-funded projects over the last several years to determine the number of patents as well as commercial and near-commercial technologies resulting from EERE funding (see Figure 11).

FIGURE 10. Patents granted to and applications filed by projects funded by the DOE Hydrogen Program.

FIGURE 11. DOE is tracking the commercial success of hydrogen and fuel cell technologies developed by EERE-funded projects. Complete results will be documented in a report by Pacific Northwest National Laboratory, *Pathways to Commercial Success: Technologies and Products Supported by the Hydrogen, Fuel Cells and Infrastructure Technologies Program*.

NEW PROJECTS SELECTED AND NEW SOLICITATIONS ISSUED

In FY 2009, the DOE Hydrogen Program competitively selected new projects to address key barriers in the development of hydrogen and fuel cell technologies. These included:

- Twenty-eight projects (approximately \$113M; \$129M with cost share over five years) in fuel cell technologies to develop novel catalysts, explore innovative concepts in materials and components, identify degradation mechanisms and mitigation strategies, understand the effects of water transport, and improve materials and packaging for portable-power fuel cells.

- Twelve projects (\$41.9M over two years; \$114.3M with cost share) to support the deployment of nearly 1,000 fuel cell systems for emergency backup power and material handling applications (e.g., forklifts), as well as the demonstration of fuel cells for residential combined heat and power, auxiliary power units, and portable applications. These projects were funded under the American Recovery and Reinvestment Act of 2009.
- Initiation of the competitively selected Hydrogen Storage Engineering Center of Excellence (\$40M over five years) to provide a coordinated approach to the engineering R&D of on-board storage and refueling systems.

INTERNATIONAL ACTIVITIES

International Partnership for the Hydrogen Economy

The United States is a founding member of the International Partnership for the Hydrogen Economy (IPHE), which includes 16 member countries (Australia, Brazil, Canada, China, France, Germany, Iceland, Italy, Japan, New Zealand, Norway, South Korea, Russia, the United Kingdom, and the United States) and the European Commission. The IPHE is a forum for governments to work together to advance worldwide progress in hydrogen and fuel cell technology research, development, and deployment. IPHE also offers a mechanism for international R&D managers, researchers, and policymakers to openly share program strategies.

Since its inception, the IPHE has endorsed a total of 31 collaborative projects that cover a broad range of topics including hydrogen production, hydrogen storage, fuel cell technology, demonstration of fuel cell technology in light-duty vehicles and buses, and the socio-economic impacts of hydrogen production. In 2008, the IPHE published the “Hydrogen and Fuel Cell Brief for Policymakers” and initiated three new global IPHE projects focusing on Hydrogen Highways, Renewable Hydrogen Production, and an International Youth Competition.

The IPHE’s priorities are follows:

- Accelerating the market penetration and early adoption of hydrogen and fuel cell technologies and supporting infrastructure.
- Encouraging policy and regulatory actions to support widespread deployment.
- Raising the profile of hydrogen with policy-makers and the public.
- Monitoring hydrogen, fuel cell, and complementary technology developments.

For more information, please visit www.iphe.net.

International Energy Agency

The United States is also involved in international collaboration on hydrogen and fuel cells through participation in the International Energy Agency (IEA), where it is a member of both the Advanced Fuel Cells Implementing Agreement (AFC) and the Hydrogen Implementing Agreement (HIA). These agreements provide a mechanism for member countries to share the results of research activities in their respective areas.

The IEA AFC currently comprises six tasks: Molten Carbonate Fuel Cells, Polymer Electrolyte Fuel Cells, Solid Oxide Fuel Cells, Fuel Cells for Stationary Applications, Fuel Cells for Transportation, and Fuel Cells for Portable Power. The HIA is also in the process of defining a new task on Large Scale Hydrogen Infrastructure and Mass Storage. The participating countries are Australia, Austria, Belgium, Canada, Denmark, Finland, France, Germany, Italy, Japan, South Korea, the Netherlands, Norway, Mexico, Sweden, Switzerland, Turkey, the United Kingdom, and the United States. The United States participates in all of the AFC’s tasks except Fuel Cells for Portable Power. The implementing agreement was recently extended from 2008 to 2013. Information about the IEA Advanced Fuel Cells Implementing Agreement is available at www.ieafuelcell.com.

The IEA HIA is focused on RD&D and analysis of hydrogen technologies. It includes nine tasks: Integrated Systems Evaluation & Analysis, Hydrogen Safety, Biohydrogen, Fundamental and Applied Hydrogen Storage Materials Development, Small-Scale Reformers for On-site Hydrogen Supply, Wind Energy and Hydrogen Integration, High-Temperature Production of Hydrogen, Advanced Materials for Hydrogen from Waterphotolysis, and Near-Market Routes to Hydrogen by Co-Utilization of Biomass with Fossil Fuel. The United States participates in all of these tasks. Members of the HIA are Australia, Canada, Denmark, the European Commission, Finland, France, Germany, Greece, Iceland, Italy, Japan, South Korea, Lithuania, the Netherlands, New Zealand, Norway, Spain, Sweden, Switzerland, Turkey, the United Kingdom, and the United States.

As part of the Integrated Systems Evaluation task, the IEA HIA completed a number of case studies³ in hydrogen systems that synthesized lessons learned and technology operating experience. These case studies, including a proposed hydrogen power station with carbon capture in the United Kingdom, the EPACOP project (Expérimentation de 5 Piles A Combustible sur sites OPérationnels) in France to test proton exchange membrane fuel cells under “real world” conditions for residential and commercial applications, and a hydrogen house in Italy, provide the DOE Program insight into progress made by other member countries.

OTHER PROGRAM ACTIVITIES

Market Transformation

In FY 2009, the Program increased its focus on a new activity - “market transformation” - to help promote the widespread commercialization of fuel cell power systems. The goals of this effort are to increase opportunities for market expansion, gather valuable data from the operation of fuel cells in integrated systems in real-world conditions, eliminate non-technical barriers such as codes and standards, accelerate user acceptance, help companies bridge the “valley of death” between development and commercialization, and enable agencies to meet energy efficiency goals. The Program actively collaborates with other agencies to facilitate federal deployment of fuel cells in key early markets (including specialty vehicles, material handling equipment, backup/remote power, and prime power for critical applications), as well as integrated renewable hydrogen production projects. Federal agency partnerships are supported by the Hydrogen and Fuel Cell Interagency Working Group and Task Force.

By purchasing fuel cells to meet their energy needs, federal agencies can play a role in reducing technology cost, developing and sustaining a domestic supplier base and in increasing public awareness of the technologies. The Program continues to collaborate with federal agencies to deploy fuel cells at federal sites across the country. The Program initiated projects to install 43 emergency backup power systems at the Federal Aviation Administration and Department of Defense (DOD) sites, and collaborated with the Defense Logistics Agency (DLA) to deploy 40 material handling units. Plans are in place for DLA’s installment of 60 more units at three additional sites across the country. The Program is also planning to deploy up to 75 emergency backup power units in collaboration with the Army Construction Engineering Research Laboratory, the National Park Service, the Ohio National Guard, and several other DOD sites. In addition, the DOE National Laboratories are performing feasibility studies examining the installation of stationary fuel cell systems at their facilities. Studies will be completed at the National Renewable Energy Laboratory, Oak Ridge National Laboratory, Pacific Northwest National Laboratory, Argonne National Laboratory, Sandia National Laboratories, Thomas Jefferson National Accelerator Facility, and the Y12 National Security Complex.

American Recovery and Reinvestment Act Projects

The Program initiated new projects in FY 2009 under the American Recovery and Reinvestment Act (Recovery Act). Twelve projects will receive \$41.9 million of Recovery Act funds for the deployment of more than 1,000 fuel cells for emergency backup power and material handling applications (e.g.,

³ IEA HIA Web site, www.ieahia.org/page.php?s=d&p=casestudies.

forklifts), as well as the demonstration of fuel cells for residential combined heat and power, auxiliary power units, and portable applications.

These deployments will have significant near-term impact, creating jobs in fuel cell manufacturing, installation, maintenance and support service sectors. Industry participants have reinforced their commitment by proposing approximately \$72.4 million in cost-share—bringing total project funding to nearly \$114.3 million.

Hydrogen Quality

The quality of hydrogen fuel is expected to play a large role in the ultimate performance, durability, and cost of fuel cell systems. Higher quality fuel allows for lower fuel cell system costs, while higher fuel quality requirements correlate to higher lifecycle costs for hydrogen production, purification, distribution, storage, and detection systems. To quantify these relationships and to develop a roadmap to define R&D priorities in this cross-cutting area, DOE established the Hydrogen Quality Working Group, which includes participants from the automotive and energy industries, the national laboratories, and the DOE Hydrogen Program.

The Hydrogen Quality Working Group continues to develop and refine models and tools to analyze the tradeoffs for hydrogen production and fuel cell performance based on various levels of hydrogen quality. The Working Group has developed a model of the pressure-swing adsorption hydrogen purification system and assessed the effect of allowable CO concentrations on hydrogen production costs. While reducing CO concentration in hydrogen fuel is not expected to significantly impact the cost of hydrogen production, the cost of measuring CO concentrations at the proposed low levels of 0.1 ppm can increase the dispensed cost of hydrogen significantly. Work continues to develop this model further and to seek experimental verification of the results.

Coordination with Vehicle Technologies Program

In FY 2009, three key activities—Technology Validation; Education; and Safety, Codes and Standards—were funded through EERE’s Vehicle Technologies Program and closely coordinated with the Office of Hydrogen, Fuel Cells and Infrastructure Technologies. The Technology Validation activity continued its Learning Demonstration with 140 hydrogen fuel cell vehicles and 20 hydrogen stations. The Program has now demonstrated more than 2.2 million miles of real-world driving and more than 90,000 kg of hydrogen dispensed since its inception. Data shows efficiencies of 53-58%, a driving range of up to 254 miles, and durability of roughly 2,000 hours. The Safety, Codes and Standards activity continued to make progress in facilitating the development of codes and standards and conducting the underlying safety research to ensure the safety of hydrogen and fuel cell technologies. The Education activity continued its efforts in state and local government outreach; education related to early deployment; and university programs. More details on these three activities can be found at: http://www1.eere.energy.gov/vehiclesandfuels/resources/proceedings/2009_merit_review.html.

FIGURE 12. Recovery Act projects and proposed funding to deploy fuel cells. DOE funding has supported R&D resulting in the success of the fuel cell suppliers involved in all these projects.

Company	Application
Delphi Automotive	Auxiliary Power
FedEx Freight East	Specialty Vehicle
GENCO	Specialty Vehicle
Jadoo Power	Backup Power
MTI MicroFuel Cells	Portable Power
Nuvera Fuel Cells	Specialty Vehicle
Plug Power, Inc. (1)	CHP
Plug Power, Inc. (2)	Backup Power
Polyfuel, Inc./UNF	Portable Power
ReliOn Inc.	Backup Power
Sprint Communications	Backup Power
Sysco of Houston	Specialty Vehicle

CHP - Combined Heat and Power

EXTERNAL COORDINATION, INPUT, AND ASSESSMENT

DOE Utilizes Expertise from the Stakeholder Community and Government Partners

Hydrogen and Fuel Cell Technical Advisory Committee. The Hydrogen and Fuel Cell Technical Advisory Committee (HTAC) was created in 2006 to advise the Secretary of Energy on issues related to the development of hydrogen and fuel cell technologies and to provide recommendations regarding DOE's programs, plans, and activities, as well as safety, economic, and environmental issues related to hydrogen. HTAC members include representatives of domestic industry, academia, professional societies, government agencies, financial organizations, and environmental groups, as well as experts in the area of hydrogen safety.

The HTAC met three times between August 2008 and August 2009. As required by the Energy Policy Act of 2005, the Secretary's biennial report to Congress is scheduled for release in 2010, describing HTAC's recommendations, addressing how DOE will implement those recommendations, and providing an explanation for those recommendations that will not be implemented.

Federal Agency Coordination—the Interagency Task Force and the Interagency Working Group. The Interagency Task Force (ITF), consisting of senior-level representatives from 15 agencies, plays a critical role in supporting and enhancing the market introduction of new technologies by focusing on federal leadership in early adoption of fuel cell technologies. This year, the ITF convened once to discuss agency demonstration and deployment activities and plans. As a result of the transition to the new administration, new appointees to each participating agency must be identified. The next meeting will be held once the new appointees have been confirmed.

Underpinning the ITF, the staff-level Hydrogen and Fuel Cell Interagency Working Group (IWG), co-chaired by DOE and the White House Office of Science and Technology Policy, meets monthly to share expertise and information about ongoing programs and results, to coordinate the activities of federal entities involved in hydrogen and fuel cell RD&D, and to ensure efficient use of taxpayer resources. The IWG's public Web site, www.hydrogen.gov, serves as a portal to information about all federal hydrogen and fuel cell activities, programs, and news.

National Academy of Sciences. The National Research Council (NRC) of the National Academies provides ongoing technical and programmatic advice to the DOE Hydrogen Program. The NRC has conducted independent reviews of both the Program⁴ and the research and development activities of the FreedomCAR and Fuel Partnership.^{5,6} The NRC's two reviews of the Partnership to date have offered recommendations on the Partnership's technical direction, strategies, funding, and management. In parallel with the second review of the Partnership, the NRC also conducted a study to determine the investments in R&D, demonstrations, government actions, education, and infrastructure that will be required for the development of fuel cell technologies and for the successful transition from petroleum- to hydrogen-fueled vehicles in a significant percentage of the U.S. vehicle market by 2020, along with potential reductions in oil use and CO₂ emissions.⁷ While the study also investigated the impact of alternative measures such as improved fuel economy, increased penetrations of hybrid vehicles and the use of biomass-derived fuels, plug-in hybrid vehicles were originally not taken into consideration.

⁴ National Research Council and National Academy of Engineering, Committee on Alternatives and Strategies for Future Hydrogen Production and Use, *The Hydrogen Economy: Opportunities, Costs, Barriers and R&D Needs*, (Washington, D.C.: National Academies Press, 2004).

⁵ National Research Council of the National Academies; Committee on Review of the FreedomCAR and Fuel Research Program, Phase 1; Board on Energy and Environmental Systems, Division on Engineering and Physical Sciences, Transportation Research Board; *Review of the Research Program of the FreedomCAR and Fuel Partnership: First Report*, (Washington, D.C.: National Academies Press, 2005).

⁶ National Research Council of the National Academies; Committee on Review of the FreedomCAR and Fuel Research Program, Phase 2; Board on Energy and Environmental Systems, Division on Engineering and Physical Sciences, Transportation Research Board; *Review of the Research Program of the FreedomCAR and Fuel Partnership: Second Report*, (Washington, D.C.: National Academies Press, 2008).

⁷ National Research Council of the National Academies; Committee on Assessment of Resource Needs for Fuel Cell and Hydrogen Technologies; Board on Energy and Environmental Systems, Division on Engineering and Physical Sciences; *Transitions to Alternative Transportation Technologies: A Focus on Hydrogen*, (Washington, D.C.: National Academies Press, 2008).

The NRC has initiated a follow-on study to investigate the potential impact of plug-ins, to be released in late 2009. As part of these efforts, the NRC has met with battery developers, original equipment manufacturers, utilities and analysts to gather information on the technology.

DOE has addressed the recommendations from all of the NRC's reviews and incorporated many of them into the Program and Partnership activities. Currently, the NRC is conducting the Phase III review of the Partnership, to review technical goals, evaluate progress, and examine research activities.

FY 2009 Annual Merit Review and Peer Evaluation. In addition to soliciting feedback from these expert and stakeholder groups, the DOE Hydrogen Program holds an Annual Merit Review, which provides an opportunity for the Program to obtain an expert peer review of the projects it supports and to report its accomplishments and progress. In 2009, DOE held this review from May 18–22, 2009, in Arlington, Virginia, for the first time in conjunction with the annual review of DOE's Vehicle Technologies Program. Over 1,500 people attended the review, and 256 projects were presented, of which 216 were peer-reviewed.⁸ The Review also provides a forum for promoting collaborations, the exchange of ideas, and technology transfer. Reviewers evaluate the Program's projects and make recommendations to the principal investigators and to the Program. DOE uses these evaluations to make project funding decisions for the upcoming fiscal year. This year, there were 189 contributing reviewers—the report compiling their comments is available at www.hydrogen.energy.gov/annual_review.html. The next review will be held June 7–11, 2010, in Washington, D.C.

IN CLOSING...

We are pleased to present the U.S. Department of Energy's *FY 2009 Hydrogen Program Annual Progress Report*. The report is divided into chapters and organized by technology area (e.g., Fuel Cells, Hydrogen Storage, etc.). Each chapter opens with an overview written by a DOE Technology Development Manager that summarizes the progress and accomplishments of this fiscal year. The 256 projects outlined in this document represent the work of the many innovative scientists and engineers supported by the Hydrogen Program. It is they who are responsible for the progress reported herein and the technical accomplishments outlined above. We thank them for their hard work, commitment and continued progress.

Sunita Satyapal
Acting Program Manager
DOE Hydrogen Program
Office of Energy Efficiency and Renewable Energy

⁸ Not all of the projects presented were reviewed, because projects from the DOE Office of Science are reviewed through a process managed by the Office of Science that involves different evaluation criteria and projects that have ended are not reviewed.

II. HYDROGEN PRODUCTION

II.0 Hydrogen Production Sub-Program Overview

Introduction

The Hydrogen Production activity in Fiscal Year 2009 was focused on developing hydrogen production technologies that enable the introduction and long-term viability of hydrogen as an energy carrier for portable power, stationary power and transportation applications. A variety of feedstocks and technologies are being pursued.

Four DOE offices have been engaged in research and development (R&D) relevant to hydrogen production. The Office of Energy Efficiency and Renewable Energy (EERE) is developing technologies for producing hydrogen from bio-derived renewable liquids and by electrolysis of water, as well as centralized renewable production options that include water electrolysis integrated with renewable power (e.g., wind, solar, hydroelectric, and geothermal), biomass gasification, solar-driven high-temperature thermochemical water splitting cycles, direct photoelectrochemical water splitting, and biological processes. The Office of Fossil Energy (FE) is focused on advancing the technologies needed to produce hydrogen from coal-derived synthesis gas, including co-production of hydrogen and electricity as well as carbon sequestration. The Office of Nuclear Energy (NE) is developing hydrogen production using heat from an advanced nuclear reactor through high-temperature steam electrolysis and thermochemical water splitting cycles. The Office of Science's basic research program emphasizes fundamental understanding of biological and biomimetic hydrogen production, photoelectrochemical water splitting, catalysis, and membranes for gas separation.

Goal

Research and develop low-cost, highly efficient hydrogen production technologies from diverse, domestic sources, including coal (with sequestration), nuclear and renewable sources.

Objectives

Reduce the cost of hydrogen to \$2.00-\$3.00/gasoline gallon equivalent (gge) dispensed at the pump. This goal applies to all production technology pathways. Technologies are being researched to achieve this goal in timeframes relative to their current states of development. The dispensed cost target of several hydrogen production pathways are summarized in the following table.

Production Pathway	Production Site	Near-Term Hydrogen Cost Target		Long-Term Hydrogen Cost Target	
		Year	\$/gge	Year	\$/gge
Bio-Derived Liquids	Distributed	2014	\$3.80	2019	\$3.00
Electrolysis	Distributed	2014	\$3.70	2019	\$3.00
Biomass Gasification	Central	2014	\$3.30	2019	\$2.10
Electrolysis	Central	2014	\$4.80	2019	\$3.00
Solar Thermochemical	Central	N/A	N/A	2019	\$4.00

N/A - not applicable

- Since previous work demonstrated the \$3.00/gge cost target could be met from distributed natural gas, DOE no longer funds R&D in this area, and industry will take the lead as the market develops.
- By 2019, verify the potential for high-temperature thermochemical cycles driven by concentrated solar energy to be competitive in the long term.
- Develop advanced renewable photoelectrochemical and biological hydrogen generation technologies. By 2020, verify the feasibility of these technologies to be competitive in the long term.
- By 2016, prove the feasibility of a near-zero emissions, high-efficiency plant that will produce both hydrogen and electricity from coal and that also reduces the cost of hydrogen from coal by 25 percent compared to current technology.

FY 2009 Accomplishments

Biomass and Bio-Derived Liquids Pathways

- United Technologies Research Center exceeded 95% conversion of cellulosic biomass (yellow poplar) with 74% hydrogen selectivity.
- Pacific Northwest National Laboratory increased hydrogen yields to >92% by optimizing catalyst formulations and reaction conditions for vapor phase reforming at low pressure.
- National Renewable Energy Laboratory (NREL) completed pilot unit parametric studies and updated their Aspen Plus gasification model. With this update, the model now predicts approximately 50% less char formation, which is closer to measured values.
- NREL demonstrated partial oxidation of a 90 wt% bio-oil/10 wt% methanol mixture in a bench-scale reactor system. Non-catalytic gas-phase oxidation of bio-oil followed by catalytic reforming of the gas/vapor intermediate resulted in 85-90% carbon-to-gas-conversion.

Electrolysis

- Giner Electrochemical Systems demonstrated 1,000-hour single cell membrane activity operating at 80°C, 300 psig, 1,500 mA/cm² current density, and 75% efficiency (lower heating value, LHV). The fluoride loss rate during the test was used to project a membrane lifetime of 45,000 to 55,000 hrs.
- Giner Electrochemical Systems is testing a new biphenyl sulfone membrane which costs about half that of their current membranes. Single cell tests show 75% efficiency (LHV) under nominal operating conditions (80°C, 300 psig) and long-term durability tests are planned.
- NREL researchers developed standardized, international electrolyzer testing protocols that are currently under peer review.
- NREL conducted an independent analysis of distributed and centralized hydrogen production costs. The analysis showed an estimated cost of \$4.90 - \$5.70/gge for distributed production and \$2.70 - \$3.50/gge for central production, at the plant gate.

Solar Pathways

- NREL and the University of Colorado tested a prototype aerosol reactor for thermochemical water splitting “on-sun.”
- University of Colorado decreased the water splitting temperature by 200°C by using atomic layer deposition for the CoFe ferrite on alumina.
- Technoeconomic analysis was completed on several high-temperature thermochemical cycles resulting in the down-selection of the ZnO cycle and identification of critical tasks for the remaining cycles. Resources were redirected to the critical tasks.
- Directed Technologies, Inc. completed a boundary level technoeconomic analysis for the photoelectrochemical (PEC) direct water splitting pathway. The analysis identified several pathways to meet hydrogen production cost targets using PEC. Projected hydrogen costs range from about \$4 to \$10/gge.
- The PEC Working Group developed standardized test protocols for PEC materials. The test protocols are currently under peer review and scheduled for January 2010 publication.
- NREL conducted a Go/No-Go decision analysis and eliminated from further study the Co-Al-Fe-O PEC material class that had initially yielded promising results in combinatorial synthesis and screening tests. Resources were redirected towards synthesis and characterization of more promising carbide and nitride materials.
- University of California, Berkeley completed the cloning of the previously identified Tla2 gene. This gene enables 15% solar to chemical energy conversion in microalgae. The high conversion brings the microalgae effort halfway to the theoretical conversion maximum of 30%.
- Directed Technologies, Inc. completed a boundary level techno-economic analysis for hydrogen production cost including four different biological processes: photolytic, photosynthetic,

fermentation, and microbial aided electrolysis. In addition, the analysis evaluated an integrated approach that combined multiple processes. The results show several pathways that can meet hydrogen production cost targets in the long term with costs ranging from about \$3 to about \$12/gge.

- Penn State University and NREL developed and demonstrated an integrated system that improves hydrogen molar yield via fermentation by a factor of four to eight, surpassing the DOE 2013 target. The system uses dark fermentation of lignocellulosic corn stover followed by a microbial electrolysis cell reaction.
- NREL researchers immobilized sulfur-deprived algal cells in a polymeric, biodegradable matrix and demonstrated continuous hydrogen production for a total of 300 hours under aerobic conditions with a conversion efficiency of approximately 0.7% at low light intensity. Previous aerobic production, using suspension cultures, showed no hydrogen generation.

Fossil Energy

- The Office of Fossil Energy has developed and implemented a standardized testing protocol for membrane separations.
- Eltron Research, Inc. and Southwest Research Institute[®] have demonstrated, in bench-scale tests, membranes that have the ability to meet nearly all of FE's 2010 hydrogen separation targets. Preliminary cost estimates of the Eltron membrane show that the technology could be competitive with conventional technology. Southwest Research Institute[®] has also produced self-supported Pd-Cu alloy membranes that have reduced membrane thickness from 25 microns (2007 state-of-the-art) to 5 microns.
- The National Energy Technology Laboratory Office of Research and Development (ORD) completed independent verification testing of several membranes to validate performance. ORD has also conducted studies on the impact of sulfur on palladium membranes that have shown that two degradation mechanisms typically occur and that gas species concentrations throughout the membrane can impact degradation.
- Preliminary economic analysis show membranes have the potential for lower electricity cost, higher thermal efficiency, and improved CO₂ capture compared to conventional technologies.

Nuclear Energy

- Idaho National Laboratory operated their integrated laboratory-scale high temperature electrolysis unit for 45 days achieving 5,650 liters per hour peak output at 12 kWe input.
- Savannah River National Laboratory developed new operating methods that demonstrated electrolyzer operation without limitations caused by sulfur build-up.
- A team consisting of General Atomics, Sandia National Laboratories and the Commissariat à l'Énergie Atomique of France completed the integrated laboratory-scale Sulfur-Iodine thermochemical system operation. Hydrogen was produced at rates up to 30 to 40 liters per hour.

Budget

The FY 2009 budget for hydrogen production provided \$38.3M for continued hydrogen production research. FE received \$25M, NE \$7.5M and EERE \$5.8M to continue research efforts for FY 2009.

The President's FY 2010 budget realigns the Hydrogen Program to focus on nearer-term impacts to our Nation's most pressing energy needs. As part of the realignment, no funding for EERE and NE Hydrogen Production was requested. FE's request is \$16.4M.

2010 Plans

- Final reports documenting progress will be issued in FY 2010. The applied R&D programs in EERE and NE will coordinate with the Office of Science, which plans up to about \$50 million of basic research related to hydrogen and fuel cell technologies. Through basic science activities, a

fundamental understanding of issues related to hydrogen production, particularly in the longer term R&D areas of high temperature thermochemical, photoelectrochemical and biological processes, can help address the challenges of hydrogen production technologies. In addition, through the deployment projects funded by the American Recovery and Reinvestment Act, lessons learned related to hydrogen production technologies will be determined.

- Continue laboratory-scale research efforts on hydrogen from coal production technologies and advance hydrogen separation membrane technologies. Conduct laboratory-scale efforts on combined water-gas shift hydrogen separation systems (i.e., process intensification).

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II.A.1 Low-Cost Hydrogen Distributed Production System Development

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Contract Number: DE-FG36-05GO15026

Subcontractor:

Süd Chemie, Inc., Louisville, KY

Start Date: July 1, 2005

Projected End Date: September 30, 2009

[LHV] of fuel cell-grade hydrogen out/[LHV of fuel in + electricity in]: 70%.

- Distributed hydrogen cost from natural gas: \$2.50/kg (production capital cost component: \$0.47/kg).
- Distributed hydrogen from ethanol cost: \$3.60/kg (production capital cost component: \$0.50/kg).

Accomplishments

- Based on this extensive test experience at 113 kg/day scale, H₂Gen redesigned the SMR reactor to improve manufacturability, performance and durability.
- Started commercial production of HGM-10000 565 kg/day units.
- Demonstrated 2,700 hours of operation of the reformer on commercially available E-85 fuel in the laboratory microreactor test.
- Started development work for coated wall reformer technology.

Approach

To meet the DOE cost targets, the HGM system must be improved both in terms of higher efficiency (to cut down the cost of natural gas) and also in reduced capital cost. Furthermore, the capacity of the HGM must be increased, both to cut the cost of hydrogen (since many HGM components will scale less than linearly with increased hydrogen capacity) as well as to meet the demands of a full service fueling station. We have therefore designed, built and field-tested an HGM-10000 with five times the capacity of our current system.

While we expect that the HGM-10000 (565 kg/day) technology scaled to 1,500 kg/day will meet or exceed the DOE 2015 cost targets for the hydrogen production and gas cleanup portion of a fueling station, it will still depend on natural gas. To reach the DOE renewable hydrogen goal, we, in collaboration with our catalyst partner, Süd Chemie, also began evaluating the cost and efficiency of reforming ethanol at the local fueling station using the H₂Gen technology. We expect that hydrogen made from ethanol will be the least costly renewable hydrogen option for at least a decade or two.

Results

HGM-10000 Field Testing – Analysis of the first HGM-10000 unit performance over 3,963 hours of field operation followed by inspection and mechanical evaluation of the SMR reactor at the H₂Gen facility led

Objectives

- Design, build and test a steam methane reformer (SMR) system that will achieve the DOE cost and efficiency targets for 2015.
- Demonstrate the efficacy of a low-cost renewable hydrogen generation system based on distributed production of hydrogen from ethanol.

Technical Barriers

This project addresses the following technical barriers from the Production section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) Reformer Capital Costs
- (B) Reformer Manufacturing
- (C) Operation and Maintenance (O&M)
- (D) Feedstock Issues
- (E) Greenhouse Gas Emissions
- (F) Control and Safety

Technical Targets

- Total production system (SMR + pressure swing adsorption, PSA) efficiency (lower heating value

to an SMR reactor redesign effort to incorporate all the “lessons learned” from the unit operation. The redesign resulted in higher stress and detonation resistance in the reactor duct flow and improved manufacturability.

Two new reactors were built, one replacing the reactor on the first HGM-10000 unit and another one for the second commercial HGM-10000 unit. Both units were started in the field and went through field testing, which was performed at H₂Gen expense without DOE cost share. H₂Gen now commercially offers HGM-10000 units for sale and is in a process of completing an order for four more HGM-10000 units.

Ethanol Testing – Ethanol reforming testing in 2008/9 concentrated on demonstrating reforming of regular commercially available E-85 (15% gasoline in ethanol) fuel mix. Previous testing of neat ethanol showed very good promise in converting ethanol into hydrogen in a regular HGM SMR reactor, but regulations on distribution of rectified ethanol made this an unlikely fuel candidate. In fact, addition of 5% gasoline to ethanol is required at the point of production and 15% gasoline/85% ethanol mixture is a standard product available at the gas stations across the country. So the objective of testing was to demonstrate feasibility of reforming standard E-85 fuel without further cleaning and pre-treatment.

Two long-term aging tests were performed. The first test had the same sequence of catalysts as that used in HGM units and as previously used in neat ethanol testing. The catalyst bed was 27” long and consisted of four sections. From the top position, the first 6” of the catalyst bed was filled with pre-reforming catalyst, the next 9” catalyst bed was filled with reforming catalyst, followed by 6” catalyst bed of HGUT section (standard HGUT) and finally the bottom 6” catalyst bed was filled with HGHT catalyst (HGHT2). The test was run at 180 psig. This test had to be stopped after about 300 hours due to gradually increasing pressure drop through the tube. Inspection of the catalyst after the test showed that the catalyst severely coked in the reforming section of the catalyst bed, while the pre-reforming catalyst remained clean.

For the second test same tube geometry was used, but all the reforming catalyst was replaced by the pre-reforming catalyst (15” total) which showed good resistance to coking in the first experiment (coke was observed only in the reforming catalyst section). The test was operated under the same conditions with the same E-85 fuel. Stable performance was observed for 2,700 hours (Figure 1 shows the reformat composition, indicating complete conversion of ethanol and high hydrogen yield). After 2,500 hours rapid increase in the pressure drop across the reformer tube was observed and the test was stopped after 2,700 hours. The catalyst was coated with fibrous coke (Figure 2) which was likely

FIGURE 1. Reformat Composition in the E-85 Test

FIGURE 2. Scanning electron microscope image of the coke found in the E-85 reforming tube after the 2,700 hours aging test.

caused by an upset in water feed in the unattended overnight testing.

Dual Fuel Burner Selection – As part of the contract extension for Fiscal Year 2009, we had planned to design a full-scale HGM-type unit to run on ethanol, including any burner tests necessary to validate the design. One major complication in re-designing the HGM unit to operate on ethanol fuel was the fact that in the current HGM design a mixture of the PSA waste gas and the original fuel (natural gas or liquefied petroleum gas) is required to fuel the SMR burner. Furthermore, during the start up the burner is started on the feed fuel alone and is transitioned to burning waste gas when the PSA becomes active. Under steady-state conditions

the SMR burner fuel comprises about 70% H₂/30% CO₂ with small amount of trim raw fuel (natural gas or liquefied petroleum gas). The nozzle mix KromSchroder burners currently used in the HGM units have broad stability range and fit very well for this service as long as gaseous fuel is used for the start up and trim gas.

In the fourth quarter of 2008 we conducted a search for a dual-fuel burner capable of atomizing and firing liquid fuel (ethanol or E-85) and transitioning to operating on gaseous (H₂/CO₂) fuel augmented by liquid ethanol. Unfortunately, no major burner manufacturer would qualify a burner to run on such fuel and/or in the dual-fuel mode operation. Their concern was the potential of detonation in low flash temperature liquids, which presents a substantial safety hazard. Because the problem has safety implications, we believe that an overall change in system design to the use of natural gas or liquefied petroleum gas as a trim fuel during start and operation would be needed, with ethanol only being used to make the hydrogen itself. This obviously has some impact on the greenhouse gas emissions generated by the system, although these might be relatively small, as trim fuel usage is only a few percent of the overall heat flow in the plant. After consultations with DOE the plans for completing the detailed design of an HGM unit prototype running on ethanol were abandoned.

Development of Coated Wall Reformer – To mitigate the coking problem observed in reforming E-85 fuel, after consultation with and approval by the DOE program manager, work was refocused on development of the coated SMR tube approach. In this approach the catalyst is coated onto the wall of the reforming tube instead of being distributed as a packed bed. The potential benefits of this coated tube approach include:

1. Reduced the risk of coking – In most cases coking originates from fuel cracking on the hot, inert wall of the reformer tube. Coke then propagates to encapsulate the catalyst gradually restricting the gas flow and the heat flux through the tube. Coating the catalyst directly onto the wall of the reformer tube will reduce this risk by eliminating the hot, inert surface. In the coated tube reformer, the catalyst will be the hottest surface contacted by the reacting stream, decreasing the likelihood of fuel decomposition and increasing selectivity towards the reforming reaction. Coke formation on the section of the coated wall would result in formation of a hotter catalyst around this spot, likely leading to carbon gasification into CO or CO₂ by excess steam and, thus, reversing of the onset of coking. Higher average temperature of the catalyst coated on the tube wall relative to the packed bed catalyst will also increase tolerance to poisoning.
2. Decrease of required tube size – Direct contact between the reactor tube wall and catalyst gives much better heat transfer rate than a traditional

packed bed reactor. This in turn will result in a higher overall reaction rate and a smaller reformer for the same gas throughput, thereby reducing system cost by reducing the amount of expensive alloy tube required.

3. Minimize the pressure drop at high throughput – Placing the catalyst directly on the tube wall eliminates the flow resistance from the packed catalyst bed which leads to negligible pressure drop and the possibility of running at much higher throughputs.
4. Potential for one-step stream reforming of biomass into syngas – The open tube design of the coated catalyst SMR and high throughput rates achievable for this process can allow the residue from biomass gasification process to pass through the tube without plugging it. This may result in a one-step steam reforming of biomass to produce syngas that can be converted to pure hydrogen. In addition the syngas could also be followed by a synthesis reaction producing liquid fuels (Fischer-Tropsch diesel, methanol or dimethyl ether synthesis).

In the first quarter of 2009 an experimental plan was designed to compare coking resistance of the traditional packed bed and coated SMR tubes. The first step is a series of short-term tests aimed at assessing the risk of coking in steam reforming of natural gas and ethanol in traditional packed bed reactor and in coated wall tube reactor under varying operating conditions. Severe conditions (low steam to carbon ratio and high wall temperature at the reactor inlet) are selected to simulate conditions under which coke is likely to form. The temperature programmed oxidation technique performed on the samples immediately after the steam reforming testing is used to determine onset of coke formation. The second phase includes long-term aging tests, which evaluate long-term structural stability and coking resistance of coated wall tube under steam reforming conditions comparable to that of the regular hydrogen generation process.

Conclusions and Future Directions

Ethanol reforming work continued and long-term steady performance was demonstrated in reforming of commercially available E-85 ethanol fuel. Still coking of the packed bed reactor remained a problem. Further effort was directed towards development of the coated wall reforming reactor which has promise of higher coke resistance, tolerance to poisons, smaller size and lower pressure drop.

FY 2009 Publications/Presentations

1. Presentation to the 2009 DOE Annual Peer Review meeting.

II.A.2 Distributed Hydrogen Production from Biomass Reforming

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Project Start Date: October 1, 2004
Project End Date: Project continuation and
direction are determined annually by DOE

Objectives

- Evaluate and develop bio-derived liquid reforming technologies for hydrogen production that can meet the DOE 2017 cost target of <\$3.00/gasoline gallon equivalent (gge).
- Ethanol reforming: down-select preferred catalyst (Rh or Co) based on catalytic testing results combined with H2A analysis. Test criteria include activity, selectivity, life, and regenerability. Determine if catalyst performance at moderate temperatures meets criteria to justify scale up.
- Aqueous phase reforming: Identify and control the catalyst composition, reaction pathways, and catalyst preparation methods to enhance hydrogen selectivity, productivity, and catalyst life.

Technical Barriers

This project addresses the following technical barriers from the Production section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) Reformer Capital Cost
- (C) Operation and Maintenance (O&M)
- (D) Feedstock Issues
- (E) Greenhouse Gas Emissions

Technical Targets

For production of hydrogen from bio-derived liquids, the primary target is the cost of delivered hydrogen (non-compressed). This target is \$3.80/gge in 2012 and \$3.00 in 2017 (\$3.00/kg H₂). Our ethanol steam reforming work has especially focused on demonstrating performance under realistic conditions, especially in terms of conversion and product selectivity using realistic ethanol feed concentration and operating pressure. We have applied H2A methodology to determine these costs, leading to a down-selection from two to one primary catalyst. It is clear from the analysis that the cost of production is heavily tied to the cost of available ethanol. The cobalt-based catalyst system has the potential to meet the cost target for hydrogen production, if we can demonstrate acceptable catalyst life and regenerability.

For aqueous phase reforming, the costs targets remain the primary goal. We are not yet at the point of carrying out H2A analysis, although this has been provided by others working on this technology. For APR we are currently focusing on identifying the mechanistic pathways leading to desired and undesired products and understanding the pathways leading to catalyst deactivation. This improved understanding is expected to affect operating parameters that will lower cost of hydrogen production.

Accomplishments

Ethanol Steam Reforming:

- Demonstrated that Rh-based catalyst life can be significantly increased by operating at a significantly reduced weight hourly space velocity and balancing metal and support functions. Showed that Rh catalyst selectivity is driven by thermodynamic equilibrium, especially undesirable at elevated operating pressures.
- Quantified the performance of Co/ZnO catalyst over a range of conditions with realistic feed concentrations and conversion levels. Established substantially better performance of this catalyst at elevated pressures relative to the Rh catalyst in terms of hydrogen selectivity.
- H2A analysis based on both Rh- and Co-based catalysts indicates significant economic advantage of the Co catalyst and it has been down-selected for further work (Table 1).

TABLE 1. Rh and Co-based Catalysts compared to H2A Baseline

	PNNL-Rh	PNNL-Co	H2A Baseline
Capital Costs	\$0.51	\$0.46	\$0.58
Decommissioning Costs	\$0.00	\$0.00	\$0.00
Fixed O&M	\$0.16	\$0.16	\$0.20
Feedstock Costs	\$3.41	\$2.17	\$2.34
Other Raw Material Costs	\$0.00	\$0.00	\$0.00
Byproduct Credits	\$0.00	\$0.00	\$0.00
Other Variable Costs (including utilities)	\$0.08	\$0.05	\$0.05
Total	\$4.16	\$2.85	\$3.18

Aqueous Phase Reforming:

- Demonstrated that addition of Re to Pt/C catalyst significantly increases activity with modest decrease in H₂ selectivity.
- Provided increased fundamental understanding of the interaction between Pt and Re on carbon-supported catalyst, involving charge transfer from Pt to Re.
- Demonstrated that metal dispersion and particle size stability and therefore both catalyst performance is affected by the method of pretreating the catalyst prior to reduction (mild calcination).
- Quantified role of base addition on catalyst performance in terms of conversion and selectivity to hydrogen.

Introduction

The conversion of biomass-derived liquids to hydrogen is attractive because of the near carbon-neutral footprint and their availability in many regions of the U.S. Ethanol is an infrastructure fuel, thus it provides an avenue for early entry into distributed hydrogen. Ethanol is thermally stable, therefore steam reforming in the gas phase is practical and is our approach. Beyond ethanol, we target sugars and sugar alcohols, along with other polyols such as glycerol, again for distributed production of hydrogen. The other sugars and sugar are thermally unstable if vaporized to reforming temperatures, therefore an alternative approach based on aqueous phase reforming is practiced. We are addressing both feedstocks and technological approaches to producing hydrogen from bio-derived liquids.

Approach

Ethanol Steam Reforming

We are examining the catalytic reforming of ethanol at moderate temperatures (450-550°C). This approach provides the potential for hydrogen production using a single reactor, without the need for a subsequent water-gas shift step. The tradeoff of this approach is loss of activity compared with higher temperature reforming. The moderate temperature approach requires cost-effective, selective, active, and long-lived catalysts. We are examining and comparing precious metal (Rh) and base metal (Co) catalysts both for relative performance and for the ability of one or both to meet the hydrogen production cost targets.

Aqueous Phase Reforming

Aqueous phase reforming is becoming a recognized technology for the production of hydrogen from thermally unstable bio-derived sugars and sugar alcohols. Operation is at lower temperature (225-265°C) than ethanol reforming, placing an even greater demand on catalytic activity. The standard catalyst is platinum on carbon (Pt/C), which shows low activity but high hydrogen selectivity. Much development effort has been on catalyst modification to increase activity while preserving the good hydrogen selectivity. Addition of Re to Pt/C has been established as the leading candidate for enhanced aqueous phase reforming performance. Our approach has been to carry out detailed characterization of the Pt-Re/C catalyst in order to increase fundamental understanding of the promotional effect of Re, and as well to understand and optimize variables related to catalyst preparation, activation, and stabilization. We are also examining pH effects through the addition of

base on selectivity and performance, with the goal of increasing the overall understanding and control of the various reaction pathways available.

Results

Ethanol Steam Reforming

In our previous work, we found that Rh on ceria-based supports provided high activity for the conversion of ethanol, with gas phase selectivity toward hydrogen exceeding thermodynamic equilibrium. This catalyst, however, deactivated over relatively short time periods (approximately 100 hours). This year's studies have shown that by substantially lowering the space velocity, this same Rh-based catalyst gains significant stability (Figure 1). We have found that although operating at high space velocities could take advantage of the inherent activity of Rh, a non-negligible amount of the ethanol simply converted to acetaldehyde. Accumulation of acetaldehyde led to a condensation side reaction resulting in polymers that deactivated the catalyst. Operating at lower space velocities, the Rh function was able to convert acetaldehyde to H_2 and CO_2 , avoiding the non-desirable polymerization reaction. This is shown schematically in Figure 2. However, we found that an inherent limitation of the Rh catalyst was the formation of methane as an intermediate, and the lowest achievable methane selectivity is at the thermodynamic equilibrium value. This leads to an undesirable loss of hydrogen and is especially deleterious at elevated pressure operation. Parallel examination of a cobalt catalyst, supported on zinc oxide (Co/ZnO) has shown better performance in terms of selectivity toward H_2 and CO_2 while minimizing methane formation (below equilibrium values). This same benefit is maintained at elevated pressure operation (to 100 psig;

FIGURE 1. Performance of Rh/ $Y_{0.1}Pr_{0.2}Ce_{0.9}O_2$ catalyst at reduced space velocity, showing stable operation for over 200 hours.

Figure 3). We believe this was due to different reaction mechanisms occurring on the cobalt metal with methane formation being a side reaction. Although the inherent activity of the Co catalyst is less than Rh, the need to operate the Rh catalyst at low space velocities minimizes the actual activity and productivity differences between the two. That fact, combined with the lack of a need for a water-gas shift step, the lower methane selectivity, and lower catalyst cost all contributed to a down-selection of the Co/ZnO catalyst.

Aqueous Phase Reforming

Our aqueous phase reforming work has focused on improving the understanding of catalyst performance and reaction pathways, primarily focusing on glycerol feedstock. Glycerol is a more tractable feedstock

FIGURE 2. Schematic depiction of conversion of ethanol over Rh catalyst at high space velocity, leading to accumulation of acetaldehyde and production of undesirable coke precursors.

FIGURE 3. T = Performance of Co/ZnO catalyst as a function of operating pressure. Conditions: 450°C, S/C = 5, gas hourly space velocity = 11,000 h^{-1} , 4.7 % EtOH. Dashed lines correspond to predicted thermodynamic equilibrium concentrations.

that shows the same patterns of selectivity as do the sugar alcohols such as sorbitol, but with a significantly reduced product slate, simplifying the analysis. In previous work we have shown that the addition of Re to Pt/C increases the activity of the catalyst toward glycerol conversion, but the very high selectivity of Pt/C toward H_2 and CO_2 decreases upon addition of Re, with the resulting production of a significant level of light alkanes. A simplified reaction pathway analysis suggests that addition of Re has facilitated C-O bond cleavage, primarily dehydration, which sequentially can lead to alcohols and ultimately hydrocarbon formation. Addition of KOH to the aqueous phase feed provides a significant increase in H_2 /alkane ratio across the entire range of Re concentrations, as shown in Figure 4. We believe that the base addition deactivates acid sites that favor dehydration, although co-production of carboxylic anion byproducts occurs as a result of the parallel homogeneously catalyzed Cannizzaro reaction. Moreover, we observe catalyst deactivation which we believe to be due to formation of base-catalyzed aldol condensation products that deposit onto the catalyst surface and hinder active sites. We believe that by proper pH control with the appropriate base that the benefits of base addition without the liabilities may be realized. A major task in Fiscal Year 2009 is to gain a more basic understanding of the role of Re when it is added to Pt/C. The general understanding is that in the reduced form, Pt-Re is present as an alloy, and that the role of Re is to reduce the binding energy of CO, facilitating the adsorption and reaction of the glycerol substrate. Why Re retards CO adsorption is not fully understood, however. Work that we have carried out using in situ X-ray photoelectron spectroscopy (XPS) has indicated that in the formation of the Pt-Re alloy, electron density flows from the Pt to the Re, making Pt somewhat more electropositive, Figure 5. This is

FIGURE 4. Effect of Re loading on Pt/C catalyst activity and relative hydrogen vs. alkane selectivity in the presence of 1% KOH addition to the feed.

FIGURE 5. X-ray photoelectron spectra of Pt/C and Pt-Re/C catalysts following reduction at 280°C, indicating the transfer of electron density from the Pt to Re metal.

consistent with some recent theoretical calculations correlating higher CO adsorption strength with increasing electron density on the metal center [1].

Conclusions and Future Directions

Ethanol Steam Reforming

We have concluded that the Co/ZnO catalyst provides superior performance to the $Rh/Ce_{0.8}-Zr_{0.2}O_2$ catalyst and it has been down-selected for all future work. Remaining work with the Co catalyst will focus on catalyst life, including examination and possible verification of preliminary results indicating a significantly greater tendency of the Co catalyst to deposit filamentous carbon. Quantification of this effect and catalyst regenerability will be the focus of the work.

Aqueous Phase Reforming

- We have shown that the addition of Re to Pt/C catalyst increases activity and glycerol conversion to gas phase products, but at some loss of hydrogen selectivity relative to alkanes. Addition of 1% KOH base to the reaction mixture significantly increases hydrogen selectivity but results in some adverse effects such as carboxylate formation and catalyst deactivation. Some very preliminary results with formate base addition at lower concentrations has indicated that the deactivation of the catalyst can

be retarded with some increase in selectivity relative to the base case (no base addition). A combination of specific base effects (for example, formate may provide different chemistry from OH⁻) as well as overall pH effect are likely to be contributing to this result. In future work we intend to examine the effect of base concentration and base identity on Pt-Re/C performance with glycerol.

- Our work by XPS, along with some preliminary X-ray absorption near-edge spectroscopy studies, has shown that addition of Re to Pt results in a small shift in electron density from the Pt to the Re. Further work is required and planned to better quantify this effect, including the concentration dependence of Re and oxidation state of both Pt and Re in the presence of steam as well as syngas.

FY 2009 Publications/Presentations

1. D.L. King, Y. Wang, G. Xia, Y. Yang, D. Heldebrant, L. Zhang, and T. Peterson; "Aqueous Phase Reforming of Glycerol: Reaction Pathways, Base Effects, and Catalyst Deactivation." Presented orally at the 21st meeting of the North American Catalysis Society, San Francisco, June 2009.
2. A. Karim, Y. Su, J. Sun, V. Lebarbier, J.J. Strohm, D. King and Y. Wang; "Highly Stable Catalysts for Ethanol Steam Reforming". Presented orally at the 21st meeting of the North American Catalysis Society, San Francisco, June 2009.
3. L. Zhang, Y. Yang, G. Xia, D. Heldebrant, D. King, and Y. Wang; "Effect of Pt-Re Interaction on the Aqueous Phase Reforming of Glycerol over Pt-Re-C Catalysts". Oral and poster presentations at the 21st meeting of the North American Catalysis Society, San Francisco, June 2009.

References

1. S. Kathman, D. Mei, R. Rousseau, J. White, M. Gerber, and D. Stevens; "Computational Study of Ethanol Synthesis from Biomass-Derived Syngas Using Rh-Based Catalysts". Presented at the 21st meeting of the North American Catalysis Society, San Francisco, June 2009.

II.A.3 Hydrogen Generation from Biomass-Derived Carbohydrates via the Aqueous-Phase Reforming (APR) Process

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Contract Number: DE-FG36-05G15046

Subcontractors:

- University of Wisconsin, Madison, WI
- Archer Daniels Midland Company, Decatur, IL

Project Start Date: September 1, 2005

Project End Date: September 29, 2009

- Calculate the thermal efficiency and economics of the APR system utilizing different feed stocks (low-cost sugars, glucose, sugar alcohols).
- Compare results of techno-economic analysis with DOE Hydrogen Program goals.
- Perform fundamental catalysis review.
- Review system performance with regards to demonstration performance goals.
- Continue catalyst development to enhance hydrogen production efficiency.
- Operate reactor development pilot plant to gain information required for the initial reactor design for a 10 kg H₂/day demonstration system.
- Develop initial process flow diagram (PFD) and catalytic reactor design for a 10 kg H₂/day demonstration system.
- Re-evaluate the thermal efficiency and economics of the APR system with respect to Hydrogen Program goals utilizing H₂A.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section (3.1) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) Reformer Capital Costs
- (C) Operation and Maintenance (O&M)
- (D) Feedstock Issues
- (E) Greenhouse Gas Emissions

Technical Targets

It is believed that the APR process will provide a cost-effective and energy-efficient method to generate hydrogen from biomass. The project objective is to achieve the DOE 2012 cost target for distributed production of hydrogen from bio-derived renewable liquids of:

- H₂ Cost: \$3.80/gge.
- Feedstock Cost Contribution: \$2.10/gge.

Accomplishments

- Demonstrated hydrogenation of glucose to sorbitol at conditions that allow for simple integration with the APR process:
 - Identified detailed catalytic activity metrics.

Objectives

The objectives of the first year of this project are as follows:

- Identify candidate sugar streams (glucose), document plant integration requirements and associated economic factors.
- Develop catalyst and reactor based on the aqueous phase reforming (APR) process suitable for converting candidate sugar streams to hydrogen.
- Design a baseline hydrogen generation system utilizing the APR process.
- Calculate the thermal efficiency and economics of the baseline APR system.
- Assess the baseline APR system with respect to Hydrogen Program goals and make a Go/No-Go decision to proceed with further development of a demonstration system.

The objectives of the second and third years of this project are as follows:

- Continue to investigate catalyst, reaction conditions and reactor suitable for converting low-cost sugars to hydrogen.

- Developed detailed kinetic model.
- Techno-Economic Analysis
 - Development pathways identified to reach 2012 and 2017 goals.
 - Identified most cost sensitive aspects of the APR process.
- Catalytic Fundamentals
 - Developed detail chemical pathways of APR process.
 - Identified preferred chemical route for high efficiency production of H₂ from glucose.
 - Completed detailed review of thermodynamics.
 - Optimized operating conditions for improving H₂ yield and conversion to gas.
 - Developed method to analyze catalyst and support chemistry.
- Reactor Scale-Up
 - Scaled up APR reactor to reactor development scale.
 - Maintained H₂ yield and performance.

Introduction

The APR process allows the generation of hydrogen from biomass-derived compounds such as sugars, and sugar alcohols. This unique method generates hydrogen from aqueous solutions of these oxygenated compounds in a single step reactor process compared to the three or more reaction steps required for hydrogen generation via conventional processes that utilize non-renewable fossil fuels. The key breakthrough of the APR process is that the reforming is done in the liquid phase. The APR process occurs at temperatures (150°C to 270°C) where the water-gas shift reaction is favorable, making it possible to generate hydrogen with low amounts of CO in a single chemical reactor. Furthermore, the APR process occurs at pressures (typically 15 to 50 bar) where the hydrogen-rich effluent can be effectively purified.

While proven in the laboratory, the APR technology must be shown viable with low-cost sugars as the feedstock. This project will result in development of a catalyst system and an initial reactor design and associated PFD for the design of a 10 kg H₂/day prototype reactor system. The catalyst, reactor design and PFD will provide information that will be necessary to scale up the APR technology to a level that will allow for validation of system operation for generating hydrogen from low-cost sugar streams. The scaled demonstration system will provide the information required for scaling to commercial applications and will allow for techno-economic verification of the process. Glucose will be utilized as the model feedstock

in this project. However, the process will be capable of processing mixed sugar streams, like those being produced from cellulosic feedstocks.

Approach

This project combines the expertise of Virent Energy Systems (Virent), Archer Daniels Midland Company, and the University of Wisconsin to demonstrate the feasibility of generating high yields of hydrogen from glucose. Aqueous solutions of glucose can be fed to the Virent's novel APR process to generate a high hydrogen content reformat stream. The effluent reformat stream from the APR process can then be efficiently purified to produce high purity hydrogen utilizing pressure swing adsorption.

Results

Virent is investigating a proprietary catalytic reactor configurations that allow the conversion of high concentrations of glucose to a hydrogen-rich reformat. The biomass to hydrogen route via the APR process is detailed in Figure 1. The APR process utilizes biomass-derived compounds such as glucose to produce hydrogen. The technical approach for processing glucose consists of a hydrogenation section followed by the APR process. The hydrogenation of glucose to sorbitol, at conditions that allow for simple integration with the APR process, has been demonstrated. Additionally, detailed activity and kinetic modeling has been completed for the hydrogenation reaction. The main focus of catalytic research is focused on the use of sorbitol in the APR process to produce a hydrogen rich reformat stream.

- Detailed techno-economic analysis for the production of hydrogen from glucose via the APR process has been completed. The economic analysis identified the most cost sensitive aspects of the APR process. The largest cost component for the production of hydrogen from the APR process is

FIGURE 1. Biomass to Hydrogen via the APR Process

FIGURE 2. Intermediate Products of the APR Process

the cost of feedstock, followed by capital costs and operations and maintenance. The sensitivity of the cost of H_2 is greatest in regards to the effect of increasing the overall H_2 yield of the system. The second and tertiary cost effects consist of the feed stock concentration and reactor productivity.

Results from this cost analyses show that the 2012 DOE Target of \$3.80/gge and the 2017 DOE Target of <\$3.00/gge could be achieved with sugars at 6.4 cents per lb, the Biomass MYPP goal for cellulosic sugars cost in 2020, and continued development of the APR process. The analysis identified development pathways for the APR technology towards the 2012 and 2017 targets.

Economic-driven research continued focus on increasing H_2 yield. Fundamental reviews were completed in order to develop a detailed chemistry pathway, detailed catalyst metal and support chemistry and thermodynamic relationships. The chemistry pathway, simplified in Figure 2, details the intermediate compounds that may be produced such as alcohols, acids, ketones and aldehydes. The pathways also identified which of these intermediate components are favorable for H_2 generation and those that are undesirable. The chemistry pathways, in conjunction with the corresponding thermodynamic relationships, led to the exploration of new operating conditions. The new operating conditions led to an increase in H_2 yield and conversion to gas as detailed in Figure 3. The improvement in performance translates to a 10% decrease in H_2 cost over the past year. Overall, the cost of H_2 has been reduced by a factor of 10 over the course of the project.

Reactor scale-up activities were completed in the reactor development unit (RDU). The RDU has the capability of an active heating media, increased instrumentation for determination of heat transfer coefficients and a larger active

FIGURE 3. Improvement in Catalytic Performance

reactor section, in both diameter and length. The RDU demonstrated similar H_2 and CO_2 yield performance as the catalyst development unit along with an increase in conversion to gas as shown in Figure 4. The successful scaled up RDU will be numbered up for the design of a 10 kg/day H_2 demonstration system.

Conclusions and Future Directions

The APR technology is a promising and cost-competitive technology for the production of renewable H₂. However, technology development is still required to reach the DOE 2012 and 2017 cost targets. Virent's detailed model of the process has identified development pathways intended to reach the 2012 and 2017 goals.

Future Directions:

- Continue development of APR catalyst and reactor that converts glucose and sugar alcohols to hydrogen.
- Complete initial reactor design and associated PFD for a 10 kg H₂/day demonstration system.
- Review techno-economic performance of the APR system utilizing the updated H2A platform.
- Re-evaluate the thermal efficiency and economics of the APR system with respect to Hydrogen Program goals utilizing H2A.
- Final project reporting and close-out.

FIGURE 4. Reactor Scale-Up and Performance

FY 2009 Publications/Presentations

1. Presentation – NHA Hydrogen from Renewables Conference – September 23, 2008.
2. Presentation – DOE Hydrogen Program Annual Merit Review Meeting – May 19, 2009.

II.A.4 Investigation of Reaction Networks and Active Sites in Bio-Ethanol Steam Reforming over Co-Based Catalysts

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Contract Number: DE-FC36-05GO15033

Project Start Date: May 1, 2005

Project End Date: April 30, 2010

- To study how the observed catalyst characteristics influence the reaction pathways for:
 - Oxygenate formation.
 - Reverse water-gas shift.
 - Alkane and olefin formation.
 - Coke deposition.
 - Steam reforming.
- Determine how the chosen support material can influence metal dispersion and structure, and how it participates in:
 - Alcohol and water adsorption.
 - Spillover of species.
 - Intermediate and product formation.
- Determine methods that can tailor the catalyst surface for optimum selectivity and activity by:
 - Site blocking.
 - Chemical promotion.
 - Active site density control.
- Determine factors that degrade catalyst stability and optimize regeneration methods:
 - Pathways and active sites for coke formation.
 - Loss of surface area under reaction.
 - Metal-support interaction.
 - Sintering.

Objectives

To develop precious metal free catalysts that can operate at lower temperatures with high yields and selectivities for hydrogen steam reforming from bioethanol; acquire a fundamental understanding of the reaction networks, active sites and deactivation mechanisms of potential bioethanol steam reforming catalysts. More specifically:

- Determine the effect of catalyst synthesis methods on oxidation state, structure, metal dispersion, and particle size of cobalt-based bio-ethanol reforming catalysts using the following techniques:
 - Aqueous or organic impregnation.
 - Co-precipitation.
 - Sol-gel synthesis.
 - Organometallic synthesis.
 - Control of calcination and reduction conditions.
- Determine oxidation states and chemical structures that are present in active catalysts that are exposed to:
 - Varying pre-treatment protocols.
 - Differing levels of steam-to-carbon ratio during reaction.
 - Oxidative and auto thermal operation.
 - Different space velocities.

Technical Barriers

This project addresses the following technical barriers from the Production section (3.1.4.2.1) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) Fuel Processor Capital Costs
- (C) Operation and Maintenance (O&M)
- (D) Feedstock Issues

Technical Targets

This is a university project, which is a systematic and detailed study aimed to provide fundamental answers to questions that are not readily solved in an industrial setting. The approach is an iterative one that combines catalyst synthesis, characterization and reaction engineering studies. The results of this study will prevent interpreting erroneous information resulting from the screening of a large catalyst matrix by characterizing the parameters that lead to or inhibit the

formation of active sites for reforming. The information obtained from the proposed study will address many common problems associated with catalyst development, such as choice of materials, pre-treatment conditions, and factors controlling active site distribution, stability, and selectivity. Insights gained from these studies will be applied toward the design and synthesis of cost-effective and efficient reforming technologies that meet the DOE 2012 technical targets for hydrogen from bio-derived renewable liquids. Specific technical targets that would benefit from this study are the following:

- Production energy efficiency: 72.0%
- Contribution of production to capital cost: \$0.45/gge
- Total hydrogen cost from bio-derived liquids: \$3.80/gge

Accomplishments

- In an effort to increase the oxygen mobility of the catalysts, dopants with oxidation states lower than Ce (e.g., Ca) were used, leading to oxygen vacancies and changes in ceria lattice.
- Isotopic labeling studies provided insight for the overall reaction mechanism model, which was extended to take alternate reaction pathways into account.
- Novel synthesis techniques such as solvothermal, reverse microemulsion and colloidal crystal templating led to catalysts with much higher dispersion as well as superior catalytic performance (i.e., activity, selectivity, stability).
- Novel catalyst preparation methods utilizing reverse micro-emulsion techniques allowed for over 92% H₂ yield with high stability under more stringent conditions.
- Computational chemistry/molecular simulation studies on Co-CeO₂ systems were initiated as part of a collaborative effort.

Introduction

For hydrogen energy to fulfill its potential for protecting the environment, providing more efficient energy sources, and decreasing our nation's dependence on foreign oil, we need economical and efficient technologies for hydrogen production from renewable energy sources. Hydrogen production from ethanol through steam reforming lends itself very well to a distributed hydrogen production strategy and hence has the potential to offer solutions to problems associated with hydrogen storage and infrastructure. The bio-ethanol produced by fermentation of biomass can yield

an ethanol-water mixture already ideal for reforming without additional distillation steps. A review of the ethanol steam reforming literature shows that there is no consensus about an optimal catalyst, and a fundamental understanding of the relationships between catalytic properties and how these properties are affecting various reaction steps involved in this complex network is lacking.

The development of non-precious metal catalysts in this project will reduce the catalyst cost, while the lower operation temperatures will reduce the material cost for reactor systems and will also reduce the energy requirement for heating the feed mixture to high reaction temperatures. The catalyst will have high steam reforming activity, while being non-selective for various undesired side reactions, such as methanation, dehydration, dehydrogenation, coking, and reverse water-gas shift reaction. The high yields to be achieved will help increase the production energy efficiency. The catalytic system will have high stability and well-understood regeneration mechanisms. High stability will reduce catalyst cost by prolonging the active life span of the catalyst. The regeneration mechanisms will be useful in reactivating the catalyst, rather than discarding the deactivated catalyst. The design of such catalysts will not be possible without a thorough understanding of the relationships between the catalyst preparation parameters, their structural and molecular characteristics and their reaction performance. The understanding acquired through this study will eliminate the need for costly trial-and-error efforts and will enable design of catalytic systems with the desired characteristics.

Approach

The project encompasses examination of the cobalt-based catalyst system at every stage of its life history, from precursor stage to activation, deactivation and regeneration steps. The techniques used include catalyst synthesis studies, transient and steady-state reaction tests, and characterization using surface, bulk and molecular analysis techniques (both ex situ and in situ). The approach taken is not a consecutive execution of the tasks or steps in each task, but rather an iterative approach where the findings in one aspect of the study are utilized in a feed-back mechanism to plan, and modify the steps taken in another task. Understanding gained through molecular simulations is utilized in tailoring the catalyst surfaces for better performance.

Results

Last year's effort had led to use of low-valence dopants such as Ca in ceria matrix to increase the oxygen mobility of the Co/CeO₂ catalysts. This was achieved by creating oxygen vacancies in the ceria lattice. Characterization results showed that Ca

doping also increased the CeO_2 unit cell size. X-ray diffraction studies were used to quantify the expansion. The diffraction patterns of CeO_2 and $\text{Ca}_{0.1}\text{Ce}_{0.9}\text{O}_{1.9}$ are displayed in Figure 1. The peak broadening is a clear indication of smaller particle size. When the samples are compared, it is observed that the 28.56° peak for CeO_2 has shifted to 28.89° for $\text{Ca}_{0.1}\text{Ce}_{0.9}\text{O}_{1.9}$. Unit cell estimation based on the angles show an increase in the unit cell size from $5.4108 \text{ \AA}$ to $5.4151 \text{ \AA}$. The increase is

FIGURE 1. X-Ray Diffraction Patterns of CeO_2 and $\text{Ca}_{0.1}\text{Ce}_{0.9}\text{O}_{1.9}$

attributed to 10% calcium addition and it is in agreement with the literature [1-3].

The reaction mechanism proposed in the last annual report is extended to take alternate pathways into account (Figure 2). The isotopic labeling techniques are coupled with surface analysis to shed light to the reaction pathways on the catalyst surface. The ethanol steam reactant mixture diffuse on the surface of the catalyst, where ethanol adsorbs dissociatively on cobalt sites, thereby forming ethoxide species on the metal. Simultaneously, water adsorbs on ceria and forms hydroxyl groups (Scheme 1). The single hydrogen atom from water can follow two pathways: 1) formation of OH groups with the surface oxygens, 2) reaction with an H atom from another molecule of adsorbed water to form H_2 which leaves the catalyst surface (Scheme 3). Ethoxide species stationed on the metal move to the metal-support interface and lose another hydrogen atom, thereby forming acetaldehydes (Scheme 4). The acetate species have two alternate pathways: they may form acetone through aldol-condensation reaction and desorb from surface. This is the cause of the acetone in the reactant stream. However, acetone is encountered at very low concentrations in temperatures above $350\text{-}400^\circ\text{C}$ and the second pathway is more likely to be followed. The acetaldehyde species convert into acetate species through reaction with surface oxygen or hydroxyl groups (Scheme 5). The acetate species can follow different pathways. 1) Cobalt may cleave the C-C bond to form single carbon species (Scheme 7) and form CH_4 . The carbon-oxygen surface species

FIGURE 2. Proposed Reaction Mechanism for Ethanol Steam Reforming over Supported Co Catalysts

desorb or get further oxidized to form carbonate species. Supports with high oxygen capacity and mobility allow CO_2 to desorb from the surface (Schemes 8 and 9, First Route). 2) In the second route, if the oxygen is easily accessible to the CH_3 species, further oxidation will take place (Scheme 10) via both hydrogen subtraction and oxygen addition and formates will form on the surface through formaldehyde intermediates (Scheme 11). The catalyst surface gets regenerated through CO_2 desorption (Scheme 13) and the catalyst becomes ready for another cycle, independent of the reaction pathway taken. If the surface is highly acidic, ethanol dehydration may dominate the reaction pathway and result in the formation of H_2O and C_2H_4 which are the major precursors to coke due to polymerization, as described in Scheme 2 and 6. If the oxygen mobility in the catalyst is not high enough, the acetate species may remain on the surface and lead to coke formation, as reported earlier by Lima and Erdohelyi [4,5].

The cobalt particle size is controlled more effectively via reverse micro-emulsion technique. Surfactants are added to encapsulate the cobalt particles in a limited hydrophilic environment to increase cobalt dispersion and prevent reagglomeration at high temperatures. Tetrahydrofuran addition prevents the support from embedding the metal completely and silylation of the metal oxide support is achieved by adding hexamethyldisilazane to improve the chemical compatibility between the support surface and the organometallic micelle, to further increase the metallic dispersion. The exact technique can be found in the work of Martinez et al. [6,7]. Figure 3 shows two transmission electron microscopy images of Co/CeO_2 catalysts prepared by the reverse microemulsion method. Co_3O_4 particles are highlighted with the red circles. Around 90% of the oxides are found to have particle sizes between 6 and 7 nm. Furthermore the cobalt particles are noticeably embedded onto the surface of the ceria support, which leads to enhanced dispersion of the metal. This is due to the silylation of the metal oxide. Figure 4 shows the catalytic activity results of the Co/CeO_2 catalyst prepared by the microemulsion technique. The catalyst has over 90% H_2 yield at 350°C and above at weight hourly space velocities twice as high as those used for other catalysts. Catalysts that are kept on line over 120 hours at 400°C show no sign of deactivation. The novel synthesis technique gave much better results than the incipient wetness impregnation method.

Conclusions and Future Directions

- Oxygen mobility is enhanced with Ca doping.
- Isotopic labeling and in situ characterization provide new insights into the reaction mechanism.
- Novel synthesis techniques such as solvothermal, reverse microemulsion and colloidal crystal

FIGURE 3. High Resolution Transmission Electron Microscopy Images of Co/CeO_2 Catalyst Prepared by a Reverse Microemulsion Technique

templating led to catalysts with much higher dispersion as well as superior catalytic performance (i.e., activity, selectivity, stability).

- The effect of oxygen in the feed stream on product distribution as well as catalyst deactivation will be examined.
- Other bio-derived liquids will be used as feed.
- Collaborative molecular simulation work using density functional theory calculations will be performed and used to guide rational catalyst design.

Special Recognitions & Awards/Patents Issued

1. Ozkan, U.S., Song, H., "Hydrogen Production from Steam Reforming of Ethanol over Calcium Modified Co/CeO_2 Catalyst", (*In Process*).

FIGURE 4. Hydrogen Yield, C-Containing Product Distribution and Time-On-Stream Performance over a Co/CeO₂ Catalyst Prepared by a Reverse Microemulsion Technique

FY 2009 Publications/Presentations

Books

1. *New Catalyst Synthesis Techniques*, special issue of Topics in Catalysis, Guest editor, U.S. Ozkan, Springer Publisher, Volume: 49, 2008.
2. *Design of Heterogeneous Catalysts: New Approaches based on Synthesis, Characterization and Modeling*, Ed. U.S. Ozkan, Wiley-VCH, 2009.

Journal Articles

1. Song, H., Ozkan, U.S., "Ethanol Steam Reforming over Co-based Catalysts: Role of Oxygen Mobility" *Journal of Catalysis*, **261** 70-78(2009).
2. Song, H. and Ozkan, U.S., "The Role of Impregnation Medium on the Activity of Ceria-supported Co Catalysts for Ethanol Steam Reforming," *J. Molecular Catalysis*, submitted.

3. Song, H. Ozkan, U.S., "Changing the Oxygen Mobility in Co/Ceria Catalysts by Ca Incorporation: Implications for Ethanol Steam Reforming" *Journal of Physical Chemistry*. Invited paper. Submitted.
4. Song, H. and Ozkan, U.S., "Effect of Cobalt Precursor on the Performance of Ceria-Supported Cobalt Catalysts for Ethanol Steam Reforming," submitted to *Applied Catalysis A*.
5. Song, H., Tan, B., Ozkan, U.S., "Novel Synthesis Techniques for Preparation of Co/CeO₂ as Ethanol Steam Reforming Catalysts," submitted to *Catalysis Letters*.

Conference Presentations

1. Song, H., Zhang, L., Ozkan, U.S., "Catalytic Hydrogen Production from Bio-Derived Liquids over Non-Noble Metal Catalysts" *OAI Poster Session*, Columbus, OH, February 2008.
2. Song H., Zhang, L., Ozkan, U.S., "Hydrogen Production from Bio-derived Liquids over Cobalt-Based Catalysts",

235th ACS National meeting & exposition, New Orleans, LA, April 2008.

3. Song, H., Zhang, L., Ozkan, U.S., “Hydrogen Production from Bio-derived Liquids over Cobalt-Based Catalysts” 14th International Congress on Catalysis, Seoul, Korea, July 2008.

4. Song, H. Zhang, L., Ozkan, U.S., “Hydrogen Production from Bio-ethanol over Co-based Catalysts,” presented at the 2008 American Chemical Society Fall Meeting, Philadelphia, PA, 2008.

5. Song, H., Zhang, L., Ozkan, U.S., “Catalytic Hydrogen Production from Bio-renewable Resources” 2nd International Symposium on Bioenergy and Bioprocess Technology, Qingdao, China, October 2008.

6. Song, H., Zhang, L., Blohm, K., Ozkan, U.S., “Hydrogen Production from Bio-Ethanol Steam Reforming over Co-Based Catalysts”, 2008 AIChE Annual National Meeting, Philadelphia, PA, November, 2008.

7. Song, H., Ozkan, U.S., “Hydrogen Production from Steam Reforming of Bio-Ethanol over Non-Precious Metal Catalysts,” 21st Meeting of the North American Catalysis Society, San Francisco, CA, June 2009.

Invited Lectures

1. “Steam reforming of ethanol over Co-based catalysts: Active sites and reaction networks,” University of Berkeley, Lawrence Berkeley National Laboratory, Berkeley, CA, March 2009.

2. “Catalytic Hydrogen Production from Bio-ethanol through Steam Reforming”. USDOE Hydrogen Program Review Meeting, Washington, D.C., May 2009.

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II.A.5 Distributed Reforming of Renewable Liquids via Water Splitting Using Oxygen Transport Membrane (OTM)

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Project Start Date: May, 2005
Project End Date: Project continuation and
direction determined annually by DOE

Objectives

Develop OTM reactor that meets DOE 2017 cost target of <\$3.00/gge for producing hydrogen by reforming renewable liquids. Specific objectives for Fiscal Year 2009 were:

- Test OTMs for hydrogen production at temperatures compatible with ethanol (EtOH) reforming.
- Evaluate chemical stability of OTM during reforming of ethanol.
- Show the feasibility of reforming ethanol using OTM.

Technical Barriers

This project addresses the following technical barriers from the Production section (3.1.4) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) Reformer Capital Costs
- (B) Reformer Manufacturing
- (C) Operation and Maintenance (O&M)
- (N) Hydrogen Selectivity
- (R) Cost

Technical Targets

This project is developing compact dense ceramic membranes that transport pure oxygen to efficiently

and cost-effectively produce hydrogen by reforming renewable liquid fuels such as ethanol and bio-oil. Cost-effective small-scale reformer technology will be developed to integrate process steps, thereby minimizing unit size, capital cost, energy use, and operating cost and helping to meet DOE technical targets:

Production Unit Energy Efficiency:	72% (lower heating value, LHV) by 2012 65-75% (LHV) by 2017
Production Unit Capital Cost (un-installed):	\$1.0M by 2012 \$600K by 2017
Total Hydrogen Cost:	\$3.80/gge (delivered) at the pump by 2012 <\$3.00/gge (delivered) at the pump by 2017

Accomplishments

- Developed alternative OTMs, LSCF7328 (La-Sr-Cu-Fe-O) and SFT (Sr-Fe-Ti-O), that are suitable for ethanol reforming at low temperatures ($\leq 700^{\circ}\text{C}$).
- Increased oxygen transport rate of OTMs suitable for ethanol reforming at low temperatures ($\leq 700^{\circ}\text{C}$) by developing methods to fabricate the OTMs as thin films.
- Demonstrated chemical stability of LSCF7328 OTM during ≈ 190 h of ethanol reforming ($\approx 6\%$ EtOH in carrier gas) at 700 - 900°C .
- Analyzed ethanol conversion by OTM process at 700°C using air and steam as independent sources of oxygen for reforming.

Introduction

The goal of this subtask is to develop dense ceramic membranes that provide oxygen for the efficient and economical production of hydrogen through the reforming of renewable liquid fuels such as EtOH and bio-oil. An OTM can be used to supply high-purity oxygen from air or from oxygen produced via water dissociation. By removing oxygen as steam dissociates, an OTM enriches the retentate in hydrogen while it supplies oxygen for reforming renewable liquid fuels on the permeate side of the membrane. In this way, water splitting can produce significant amounts of hydrogen at moderate temperatures (500 - 900°C). Using steam as the oxygen source, however, requires an input of energy for water dissociation. That is one factor that favors using air as the source of oxygen for reforming with an

OTM. On the other hand, using steam allows hydrogen to be produced on both sides of the OTM. To determine which source of oxygen is the most cost- and energy-effective, a detailed system analysis must be done. In this project, we are generating the necessary data for the analysis.

Approach

In order for our approach to be cost-effective in reforming renewable liquids, an OTM must efficiently transport oxygen with either air or steam as the oxygen source. Efficient oxygen transport requires the OTM to have an appropriate combination of electronic and ionic conductivity; therefore, conductivity measurements are used to identify promising membrane materials. If a material has sufficient conductivity ($>10^{-1} \text{ ohm}^{-1}\text{-cm}^{-1}$), we measure its hydrogen production rate, which is directly related to its oxygen transport rate. In order to increase the oxygen transport rate, we decrease the OTM's thickness, coat it with porous layers to increase its active area, and modify its microstructure to overcome limitations from surface reaction kinetics. Catalysts will be used to promote reforming reactions. We measure the hydrogen production rate under various reaction conditions for periods up to $\approx 1,000 \text{ h}$ to evaluate the chemical stability of OTMs, because OTMs must be stable for extended periods to cost-effectively produce hydrogen. Because OTMs must be available in a shape with a large surface area, e.g. tubes, we fabricate small tubular OTMs and test their performance. Using steam as the oxygen source for reforming requires an energy input for water dissociation but it allows hydrogen to be produced on both sides of the OTM. In this project, we are generating the data for an independent party to conduct a detailed system analysis to determine the most cost- and energy-effective oxygen source.

Results

To make OTMs useful at temperatures compatible with reforming renewable liquids, we are developing OTMs with suitable oxygen transport rates at low temperatures ($<700^\circ\text{C}$). Although SFC2 gives the highest oxygen transport rate ($17.4 \text{ cm}^3/\text{min}\text{-cm}^2$) at 900°C , a phase transition dramatically decreases its oxygen transport below $\approx 825^\circ\text{C}$. LSCF7328 and SFT compositions have been identified as promising alternatives to SFC2. To compare the oxygen transport rates of various OTMs, we measure the rate at which hydrogen is produced by water splitting when steam flows on one side of the OTM and gas with a known hydrogen concentration flows on the other side, the so-called oxygen-permeate side. In this experiment, the OTM's oxygen transport rate is directly related to the hydrogen production rate on the steam side of the membrane.

Figure 1 compares the hydrogen production rate versus temperature for small disks of LSCF7328 and SFC2 with humidified N_2 ($p_{\text{H}_2\text{O}} = 0.49 \text{ atm}$) on the steam side of the membrane and $80\% \text{ H}_2/\text{balance He}$ on the oxygen-permeate side. At high temperatures, the hydrogen production rate of SFC2 is nearly as high as that of LSCF7328 despite the much greater thickness of the SFC2 membrane. Below $\approx 825^\circ\text{C}$, however, SFC2's hydrogen production rate drops by almost two orders of magnitude, making it unsuitable for use in this temperature range, whereas LSCF7328 shows a much more gradual decrease in hydrogen production rate.

Reducing an OTM's thickness increases its oxygen transport rate if surface reaction kinetics are not rate-limiting; therefore, we developed methods to fabricate thin-film LSCF7328 membranes on porous LSCF7328 substrates. The substrates provide structural support and enhance surface reaction kinetics. To assess the effect of porosity in the substrates, some substrates were prepared from LSCF7328 powder mixed with 20 wt% carbon while others were made without carbon. Thin films were prepared by painting porous LSCF7328 substrates with a slurry containing LSCF7328 powder, and then drying the sample at 80°C for 1 h and sintering at $1,100\text{--}1,140^\circ\text{C}$ for 10 h in air. To gauge the effect of porous Pt on the surface reaction kinetics, Pt paste was painted on the surface of some thin films and fired at 850°C for 30 min in air.

Figure 2 plots the hydrogen production rate of three LSCF7328 thin films versus $p_{\text{H}_2\text{O}}$ on the steam side.

FIGURE 1. H_2 production rate of LSCF7328 and SFC2 disks with $p_{\text{H}_2\text{O}} = 0.49 \text{ atm}$ on steam side and $80\% \text{ H}_2/\text{balance He}$ on oxygen-permeate side. Inset gives membrane thickness.

The substrates for two films were made with carbon powder (20 wt%) to increase their porosity, whereas the third film was prepared on a substrate made without carbon powder. Before they were coated with films, all substrates were fired in air for 10 h at 1,050°C. After firing, the substrate made without carbon powder was semi-porous with a relative density of 82.4%, whereas substrates made with carbon powder had a relative density of 51.2%. Of the films on substrates made with carbon, one was coated with a porous Pt layer, and one was not.

The porosity of substrates strongly affects the hydrogen production rate of LSCF7328 thin films (Figure 2). For the films without porous Pt, the hydrogen production rate for $p_{H_2O} = 0.5$ atm was 3.0 $\text{cm}^3/\text{min}\cdot\text{cm}^2$ on the denser (82.4% dense) substrate, but was 9.8 $\text{cm}^3/\text{min}\cdot\text{cm}^2$ on the more porous (51.2% dense) substrate. The film on a porous substrate that was coated with porous Pt had an even higher hydrogen production rate (11.4 $\text{cm}^3/\text{min}\cdot\text{cm}^2$), even though the film was considerably thicker (50 μm vs. ≈ 25 μm) than the un-coated film. This finding suggests that higher hydrogen production rates might be obtained by other enhancements of the surface reaction kinetics, e.g., by coating the films with porous layers of LSCF7328.

Ethanol reforming was studied at 700-900°C with two LSCF7328 thin-film disks and either air or water as the oxygen source. The ethanol partial pressure was fixed at 0.076 atm on one side of the sample by bubbling

FIGURE 2. H_2 production rate at 900°C vs. p_{H_2O} on steam side of LSCF7328 thin films on LSCF7328 substrates made with 20% carbon (51.2% dense) or without carbon (82.4% dense). Inset gives film/substrate thicknesses. 80% H_2 /balance He was flowed on oxygen-permeate side.

ultra-high purity He or N_2 through absolute ethanol at 25°C at either a “low” (200 ml/min) or “high” flow rate (800 ml/min). Either air or humidified N_2 (0.49 atm H_2O) was flowed (200 ml/min) on the opposite side of the sample. Ethanol reforming was done first at 900°C for ≈ 140 h and then at 700°C for ≈ 50 h. The products included CO, CH_4 , CO_2 , C_2H_4 , H_2 , and a trace of C_2H_6 . Un-reacted ethanol, water, and an unidentified component were also detected in the product stream, but ethanol and water were not always quantified because they were typically removed with an ice trap to prevent their condensation in the gas chromatograph. The unidentified peak could not be quantified due to its unknown origin, but we believe that it results from acetaldehyde, an idea that we will test with an acetaldehyde-bearing standard gas.

Figure 3 plots the results from ethanol reforming at 700°C. The CO_2 formation rate was negligible when water was the oxygen source, but it was considerable when air was the oxygen source. Using air, the CO_2 formation rate for one sample decreased as the flow rate increased, but it increased slightly for the other sample. Deposition of coke during the experiments might partly explain differences between the two samples, because time becomes a factor if coke deposition is involved, and the timing and sequence of measurements were not identical for the samples.

Based on the coke formation and the observed analytical results, several changes will be made in future tests. First, we will increase the water/ethanol ratio in the feed in order to reduce coke formation. Second, we will deposit a rhodium-based catalyst on the OTM in order to enhance the reaction rate between carbon-bearing species, such as CO and CH_4 , and

FIGURE 3. Products formation rates during ethanol reforming at 700°C with LSCF7328 thin-film OTM with He or N_2 (0.076 atm EtOH) flowing at a rate of 800 ml/min on one side of sample and air or humidified N_2 (0.49 atm H_2O) flowing at a rate of 200 ml/min on other side.

oxygen supplied by the membrane, while minimizing the reaction between hydrogen and oxygen. Third, we will increase the active area of the OTM in order to increase the supply of oxygen during ethanol reforming. The effect of the OTM was not large in the initial tests, because the OTM's active area was small ($\approx 1.27 \text{ cm}^2$). In the future, we will test OTM tubes with much larger active area ($>10 \text{ cm}^2$).

Conclusions and Future Directions

Significant progress was made in FY 2009 toward demonstrating the feasibility of using dense OTMs to economically produce hydrogen by reforming ethanol. Future directions include:

- Test OTMs for hydrogen production at temperatures compatible with ethanol reforming.
- Study effects of ethanol concentration, gas flow rates, OTM thickness.
- Employ catalysts to enhance the reforming of ethanol and oxygen transport.
- Generate necessary data for H₂A analysis using air and steam as the oxygen source.
- Have a third party perform detailed cost analysis to judge which oxygen source (air or steam) is more cost- and energy-effective.
- Evaluate chemical stability of the OTM for up to $\approx 1,000 \text{ h}$ during ethanol reforming at temperatures in range $550\text{--}800^\circ\text{C}$.
- Select OTM composition(s) and reaction conditions.
- Test ethanol reforming with longer OTM tubes and define suitable reforming conditions.

FY 2009 Publications/Presentations

1. Distributed Reforming of Renewable Liquids Using Gas Transport Membranes, DOE Hydrogen Program Annual Merit Review and Peer Evaluation Meeting, May 18–22, 2009. (<http://annualmeritreview.energy.gov>)

II.A.6 Distributed Bio-Oil Reforming

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Subcontractors:

- Colorado School of Mines, Golden, CO
- University of Minnesota, Minneapolis, MN

Project Start Date: October 1, 2004

Project End Date: September 30, 2012

Objectives

- By 2012, develop and demonstrate distributed reforming technology for producing hydrogen from bio-oil at \$3.80/kilogram (kg) purified hydrogen.
- By 2011, develop a prototype that incorporates the key operations: high-pressure bio-oil injection, homogeneous partial oxidation, and catalytic autothermal reforming.
- Develop the necessary understanding of process chemistry, bio-oil compositional effects, catalyst chemistry, and deactivation and regeneration strategy to form a basis for process definition for automated distributed reforming to meet the DOE targets.
- In Fiscal Year 2009, produce process performance data, including yields of hydrogen and mass balances as a function of process conditions (temperature, catalyst, oxygen-to-carbon ratio, and steam-to-carbon ratio).
- Using a bench-scale reactor system, demonstrate catalytic conversion consistent with \$3.80/kg hydrogen.

Technical Barriers

This project addresses the following technical barriers from the Production section of the Hydrogen, Fuel Cells

and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) Fuel Processor Capital
- (C) Operation and Maintenance (O&M)
- (D) Feedstock Issues

Technical Targets

TABLE 1. Distributed Production of Hydrogen from Bio-Derived Renewable Liquids

Characteristics	Units	2012 Target	2015 Target
Total Energy Efficiency	%	66	70
Production Energy Efficiency	%	72	
Storage, Compression, Dispensing Efficiency	%	94	
Total Hydrogen Costs	\$/gge	3.80	2.50

Accomplishments

- Generated hydrogen by non-catalytic and catalytic partial oxidation of bio-oil using the bench-scale reactor.
- Successfully operated the bench-scale unit using a 90:10 wt% bio-oil/methanol mixture injected to the reactor using an ultrasonic nozzle.
- Achieved 95% bio-oil to gas conversion by auto-thermal catalytic reforming (1% Rh and 1% Ce on Al₂O₃) at oxygen-to-carbon ratio (O/C) of 1.4 and steam-to-carbon ratio (S/C) of 1.7.
- Demonstrated Rh catalyst regenerability by oxidation of carbon deposits.

Introduction

Renewable biomass is an attractive near-term alternative to fossil resources because it has near zero life-cycle carbon dioxide (CO₂) impact. Recent assessments have shown that more than 1 billion tons of biomass could be available in the United States each year at less than \$50/ton [1]. This biomass could be converted to 100 million tons of hydrogen, enough to supply the light-duty transportation needs of the United States. This work addresses the challenge of distributed hydrogen production with the target of hydrogen cost

of \$3.80/kg by 2012 [2]. Pyrolysis is used to convert biomass to a liquid that can be transported more efficiently and has the potential for automated operation of the conversion system [3,4]. “Bio-oil” can then be converted to hydrogen and CO₂ in a distributed manner at fueling stations.

The thermally reactive compounds in bio-oil tend to decompose thermally and may form carbonaceous deposits and/or aromatic hydrocarbons, which are more difficult to convert to hydrogen. Thus, conventional fixed-bed reformers have not been proven efficient for this highly reactive feedstock. Reactors that fluidize or circulate the catalyst are much more suited for this application [5] but are not the optimal choice for small-scale and unattended operation. The objective of this project is to develop a system that will provide distributed production of hydrogen from bio-oil at filling stations. To accomplish this we are developing a simple fixed-bed reactor suitable for unsupervised automated operation.

Approach

Research is focused on developing a compact, low-capital-cost, low/no maintenance reforming system to enable achievement of the cost and energy efficiency targets for distributed reforming of renewable liquids. In this project, we are evaluating the following steps in the process:

- Bio-oil volatilization using ultrasonic atomization. We need to control physical and chemical properties of the liquid (viscosity), so blending with alcohol may be necessary.
- Homogeneous partial oxidation of bio-oil. We demonstrated previously that we can achieve significant conversion of revolatilized bio-oil to CO with minimal aromatic hydrocarbon formation if we keep the temperature at 650°C and oxygen concentration at a low and steady level. This stage will allow the use of an immobilized catalyst system, reduce the required catalyst load, reduce coking tendencies, and also provide some of the required heat for the process.
- Heterogeneous auto-thermal reforming of bio-oil derived gas and vapor. Non-nickel reforming catalysts, including precious metal and potential cheaper oxides and other metals that remain active, need to be examined in application to bio-oil and its partial oxidation products. Some promising target catalysts that can be used to complete the conversion of the bio-oil partial oxidation gases and vapors to hydrogen using a supported fixed bed have been identified by University of Minnesota, which works with NREL on this activity to develop less expensive catalysts that will be effective for the conversion of bio-oil-derived gas.

Initial experiments were carried out using a micro-scale continuous flow tubular reactor coupled with a molecular-beam mass-spectrometer for analyzing the product gas composition. This year, we conducted a series of tests using a bench-scale reactor system that allowed for a longer-duration steady-state operation and provided more reliable data for mass balance calculations.

Results

The micro-scale non-catalytic partial oxidation experiments were completed. In most of the tests, a 1:1 (weight) bio-oil:methanol solution was used as the feedstock, the process temperatures varied between 625 and 850°C, and a gas residence time was about 0.3 s. The effective O:C ratio was varied from pyrolysis conditions (0.7 for the 1:1 mixture) to a maximum of ~1.6. The effective O:C ratio includes oxygen present in organic molecules of bio-oil and methanol as well as that introduced as O₂, but not oxygen in water because it was not reactive under these conditions. The maximum hydrogen yields (~25%) were obtained at effective O:C ratios between 1.4 and 1.6. Similarly, the maximum yields of carbon monoxide (75-80%) were produced over nearly the same range of effective O:C ratios (1.5 to 1.6). Both hydrogen and CO were nearly constant with temperature in the studied range as shown in Figures 1 and 2. Mass balance calculations showed that for O:C of 1.4, 7-10% of bio-oil carbon was converted to carbon dioxide, 8-10% to methane, 1.5-2.5% to benzene, and 4-6% formed solid residues. It confirmed that non-catalytic partial oxidation is an effective first step for producing hydrogen from bio-oil but needs to be followed by the catalytic reforming and water-gas shift to optimize the process yield.

FIGURE 1. Yields of Hydrogen Produced by Non-Catalytic Partial Oxidation of Bio-Oil

FIGURE 2. Yields of Carbon Monoxide Produced by Non-Catalytic Partial Oxidation of Bio-Oil

The micro-scale tests of partial oxidation followed by catalytic steam reforming using a rhodium catalyst provided by University of Minnesota were carried out for bio-oils produced from different biomass feedstocks. This work was also supported by Chevron. Catalytic partial oxidation (POX)/steam reforming produced in most cases 7-10 g hydrogen per 100 g bio-oil. Bio-oils

from herbaceous feedstock were more difficult to process and left more deposits than wood bio-oils.

The bench-scale partial oxidation and steam reforming tests were carried out in the systems shown in Figure 3. The experiments used 90% bio-oil solution in methanol as the feedstock. Both partial oxidation and POX/steam reforming tests were performed using the rhodium catalyst from University of Minnesota. The bio-oil was fed to the reactor at 60 g/h, and the methane-equivalent volumetric space velocity was 30,000 h⁻¹ (compared to 2,000 h⁻¹ used for industrial steam-methane reforming). Process performances were determined at varied temperature, O/C and S/C. Gas composition at different process conditions is shown in Figure 4.

Bio-oil to gas conversion for catalytic POX/steam reforming approached 95%. Though some carbon deposits formed and slowly deactivated the catalyst, regeneration by air oxidation restored its full activity.

Conclusions and Future Directions

- The results presented in this work show that a significant amount of bio-oil conversion can be achieved in a non-catalytic partial oxidation step. The products of this step can then be catalytically converted to produce high yields of hydrogen.

FIGURE 3. Schematic of the Bench-Scale Auto-Thermal Reforming System

FIGURE 4. Gas Composition from POX of Bio-Oil at Different Process Conditions

- Bio-oils from herbaceous feedstock were more difficult to process and left more deposits than wood bio-oils.
- Initial results from bench-scale catalytic partial oxidation and steam reforming of bio-oil are very encouraging. A rhodium catalyst in a fixed-bed reactor showed a very good performance and full regenerability by air oxidation.
- Long-duration tests continue to demonstrate catalyst long-term performances.
- We initiated tests with lower-cost (nickel-based) catalysts that reduce the capital cost of the process.

FY 2009 Publications/Presentations

1. Marda, J., DiBenedetto, J., McKibben, S., Evans, R., Czernik, S., French, R., and Dean, A., Non-Catalytic Partial Oxidation of Bio-Oil to Synthesis for Distributed Hydrogen Production. *International Journal of Hydrogen Energy* (accepted for publication).
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II.A.7 Pressurized Steam Reforming of Bio-Derived Liquids for Distributed Hydrogen Production

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Project Start Date: October 1, 2005
Project End Date: Project continuation and
direction determined annually by DOE

Objectives

The objective of this work is to develop an efficient distributed hydrogen production process by:

- Using bio-derived liquids, such as ethanol, as the feedstock.
- Using pressurized steam reforming to reduce the hydrogen compression penalty.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) Fuel Processor Capital Costs
- (E) Greenhouse Gas Emissions
- (H) System Efficiency

Technical Targets

This project is conducting fundamental studies to define feasible pathways, that can meet DOE targets for efficiency, using the pressurized reforming of bio-derived liquids such as ethanol and glycerol, through the use of systems analysis and experimental evaluations of advanced reactor concepts that combine reactions with separations. The following are some of the relevant DOE targets:

Characteristics	Units	2012 Target	2017 Target
Production Unit Energy Efficiency	% (LHV)	72.0	65-75
Total Hydrogen Cost	\$/gge	3.80	<3.00

LHV - lower heating value

Accomplishments

- Two process models were set up to compare the efficiencies and their relative merits when the process is conducted at elevated (> 20 atm) pressures:
 - A catalytic steam reformer (SR) followed by a pressure swing adsorption (PSA) process.
 - A catalytic SR conducted in a (H_2 -permeating) membrane reactor (steam reformer membrane, SR-M).
- Demonstrated process options and conditions where hydrogen-permeating membrane reactor systems can exceed the efficiency achievable with the SR-PSA system.
- Identified the key challenges for the SR-M systems that can be addressed through advances in the membrane technology, i.e., flux and cost.

Introduction

Distributed hydrogen production facilities will need to store and transport hydrogen at pressures in excess of 400 atm. Existing production pathways based on natural gas produce compressed hydrogen in two compression steps: 1) the natural gas feed is compressed to the reforming pressures (10-20 atm), and 2) the final product hydrogen from the PSA unit is then compressed to the delivered pressure of ~400 atm. The energy needed for the compression can be equivalent to a significant fraction of the LHV of the product hydrogen. In this project, we are investigating the option of steam reforming a bio-derived liquid (e.g., ethanol, etc.) at elevated (>20 atm) pressures, since this pathway can greatly reduce the energy cost of hydrogen compression by feeding in a pressurized liquid stream into the reformer.

The challenges of high-pressure reforming of ethanol include (1) the thermodynamic equilibrium that favors higher methane and lower hydrogen yields at high pressures (at a given temperature and steam-to-

carbon ratio), and (2) the potentially higher capital cost associated with pressurized equipment. On the other hand, the high-pressure process offers the advantages of a more compact system (greater reactivity) and higher driving force for pressure-based separation/purification systems. The system design needs to balance these diverse characteristics to be able to deliver the hydrogen at the final pressure at high efficiencies and cost. This project has experimentally established the effect of pressure, temperature, space velocity and steam-to-carbon ratio on the product yields during the steam reforming process. The beneficial effect of hydrogen extraction through a membrane on the yields has been quantified. Alternative processes based on novel approaches, such as the use of membranes (for H₂, CO₂, O₂, etc.), or energy recovery (thermal integration, turbines, etc.) are explored in this project to identify promising options and addressing technical challenges.

Approach

A systems analysis was conducted to evaluate the benefits of a process that conducts the steam reforming of a bio-derived liquid (ethanol was used in this study) in a high-pressure catalytic reformer fitted with a hydrogen transport membrane (SR-M). The efficiency of such a system was compared to an ethanol fueled hydrogen production plant, similar to industrial systems that are fueled by natural gas for commercial hydrogen production and supply. The reference system consists of a catalytic SR followed by a PSA system for hydrogen purification (SR-PSA).

The models for the two systems were set up using MATLAB and equilibrium calculations. The calculations for the reformer in the SR-M system were done by setting up a physical model of the reactor that allowed the spatial characterization of the reaction and hydrogen permeation as functions of the temperature and partial pressures on both sides of the membranes.

Results

The system diagram for the reference case, SR-PSA, is shown in Figure 1. The ethanol-water mixture is vaporized and preheated before entering into the steam reformer. The products (reformat) exits with the species at chemical equilibrium at the reactor temperature. The reformat is cooled to 375°C and reacted in the water-gas shift (WGS) reactor. After cooling and dehumidification, the reformat enters the pressure swing adsorption unit at 40°C. The high purity hydrogen emerges from the PSA at the system pressure (the SR, WGS, PSA are all at the same pressure) and is then compressed to the final pressure of 425 atm. The percent hydrogen recovery in the PSA was specified between 70-80%. The tail gas containing the carbon oxides and methane are combusted in the burner to

generate heat for the reformer. If the energy content in the tail gas is insufficient to meet the needs in the reformer, supplemental ethanol is combusted in the burner. The efficiencies for the system (for hydrogen delivered to the final pressure of 425 atm) have been defined as,

$$Efficiency, \% = \frac{LHV_{H_2} \times 100}{LHV_{EtOH} + \left(\frac{Energy_{Electrical} + Energy_{Compressor}}{\eta_{grid}} \right)}$$

where η_{grid} , the efficiency of the grid electricity, was assumed to be 32.5% [1].

The schematic for the SR-M system is shown in Figure 2. As in the reference case, the ethanol and water streams are fed into the reformer. The membrane in this reformer separates a fraction of the hydrogen from the reforming zone, where the actual moles of hydrogen that permeate across depend on the hydrogen partial pressures across the membrane and the available surface area. The raffinate stream, containing the remaining hydrogen, carbon oxides, hydrocarbons, and steam are expanded in a turbine and then combusted in the burner to generate heat for the reformer. The permeate side pressure is an assigned (assumed) parameter. The permeated hydrogen is cooled and then compressed to the final pressure. The turbine power available from the raffinate expansion is used to offset the power needed to compress the hydrogen.

Figure 3 plots the efficiency of the SR-M as a function of the reactor pressure, at two reactor temperatures, 650°C and 800°C. The efficiencies are found to increase with pressure and can approach 70% at 80 atm and 800°C. These results reflect the assumptions/constraints of 50 ft² membrane area, 250 scfh/ft² hydrogen flux. For comparison, the reference system was exercised at two benchmark points, as shown in Table 1. These two benchmark points are also represented (dotted lines) in Figure 3, showing that the advantage of the membrane system becomes more evident at the higher temperatures and pressures.

TABLE 1. Efficiencies at two benchmark scenarios for the reference system (SR-PSA)

Bench Mark	S/C	T	P	H ₂ Recovery in PSA	Efficiency at P (atm)	Efficiency at 425 atm
		°C	atm	%	%	%
A (SR-PSA Ref.1)	3.4	750	8.0	70	70.1	59.9
B (SR-PSA Ref.2)	3.0	800	17.5	80	74.4	65.2

Qualitatively, the membrane system is simpler in that it does not require a WGS reactor and the PSA unit

FIGURE 1. Schematic of the reference case system (SR-PSA) based on the steam reforming of a bio-derived liquid.

FIGURE 2. Schematic of the membrane reactor system (SR-M) based on the steam reforming of a bio-derived liquid in a hydrogen permeating membrane reactor.

FIGURE 3. Total system efficiency for the production of hydrogen (425 atm) from ethanol.

and, barring any pin holes in the membrane, delivers the highest purity hydrogen. The disadvantage is that the hydrogen on the permeate side is at a lower pressure and has to be recompressed. Nevertheless, the efficiency calculations show that this loss can be more than offset at the higher temperatures and pressures. Practical issues such as the durability and cost of the reactor and membrane, especially at the high temperature-pressure combinations, are issues that will require resolution.

Conclusions and Future Directions

- A systems analysis was conducted to evaluate the efficiency potential of a process based on the high pressure steam reforming membrane reactor (SR-M), for the production of hydrogen from bio-derived liquids.
- Even though the permeated hydrogen is at a lower pressure, a turbo-compressor can be used to recover the compression energy from the raffinate.
- The SR-M system has higher efficiencies (than the SR-PSA benchmarks), especially at the higher temperatures and pressures.
- The analysis will continue to evaluate other process options, especially those that maintain the hydrogen at the elevated operating pressure. These include the transport of CO_2 across a membrane within the reformer to offset the negative aspects of pressurized reforming and reformat purification using PSA. The most favorable approach will then be pursued further by addressing the key technical challenge that limits the pathway to industry participation and commercial feasibility.

FY 2009 Publications/Presentations

1. Lee, S.H.D., Papadimas, D., Wu, C-H, Ahluwalia, R.K, "Pressurized Steam Reforming of Bio-Derived Liquids for Distributed Hydrogen Production," poster presentation at the 2008 Fuel Cell Seminar, Phoenix, AZ.

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II.A.8 Analysis of Ethanol Reforming System Configurations

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Project End Date: June, 2009

Program Multi-Year Research, Development and
Demonstration Plan:

Distributed Hydrogen Production from Natural Gas or
Renewable Liquid Feedstocks:

- (A) Reformer Capitals Costs
- (B) Reformer Manufacturing

Hydrogen Separations:

- (R) Cost

Technical Targets

This project entails conducting configuration and cost analysis of current and future technology distributed bio-derived liquids reforming systems for the on-site production of hydrogen. Insights gained from these studies may be applied toward future system development that can meet the DOE 2017 targets for hydrogen production from bio-derived liquids.

Objectives

- Assess cost of H₂ from bio-derived liquids:
 - Focus on 1,500 kgH₂/day distributed production forecourt systems.
 - Consider both “conventional” and “advanced” systems.
 - Conduct basic sensitivity analysis on the above reformation systems to assess the impact on H₂ cost.
- Reflect recent research:
 - Interact with DOE labs and contractors.
 - Researchers to suggest catalysts composition, performance, potential configurations.
 - Grounded in reality but with a focus on technical targets.
- Output of work is:
 - System/configuration definition.
 - Performance specification and optimization.
 - Capital cost estimation.
 - Projected hydrogen cost (\$/kg).

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section (3.1.4) of the Hydrogen, Fuel Cells and Infrastructure Technologies

TABLE 1. DOE Technical Targets

Characteristic	2006	2012	2017
System Efficiency	70%	72%	65-75%
Production Unit Capital Cost (uninstalled)	\$1.4M	\$1.0M	\$600k
Total H ₂ Cost	\$4.40/kg	\$3.80/kg	<\$3.00/kg

Accomplishments

- Defined 21 different system configurations with a wide variety of approaches.
- Designed and analyzed an annular heat exchange reactor as an alternative to the conventional tubular reformer. A detailed and highly adjustable physical configuration model was constructed and used to determine appropriate reactor sizing and cost.
- Developed kinetics models of the reforming and water-gas shift (WGS) reactors to estimate reactor bed sizes.
- Developed a 1-dimensional, non-reacting chemistry model of a metal membrane separation unit to estimate membrane surface area requirements.
- Developed a detailed but modular sizing and costing model to handle each of the 21 system configurations.
- Postulated, developed, and analyzed multiple membrane/reformer/WGS systems.

- Developed HYSYS^{®1} performance models for each system configuration.
- Completed capital cost analyses of the system configurations.
- Conducted literature reviews and interacted with industry to vet analysis.

Introduction

Small-scale distributed reforming of ethanol is one of the most promising renewable hydrogen production pathway options for the near and mid-term. It offers the potential for both relatively low-cost H₂ and scalability to small production rates appropriate to the early years of the H₂ economy. However within the class of distributed reforming systems there is considerable diversity and uncertainty regarding optimal choice of feedstock, conversion process, efficiency, and capital cost. A systematic approach needs to be developed as a tool to manage this area of the DOE Hydrogen Production program element.

The objective of this project was to examine forecourt ethanol reforming systems in sufficient detail to authoritatively estimate the performance and capital costs of the systems and thereby estimate the cost per kg of hydrogen created by the systems. Since there are multiple approaches to the conversion of the ethanol feedstock into hydrogen, a baseline system and advanced alternative configuration systems were all assessed. The overall objective of the project was to clearly define and document the performance and expected costs of leading near-term and advanced longer-term ethanol reformation systems as they pertain to small-scale (~1,500 kg/day) forecourt hydrogen production systems.

Approach

This project sought to quantitatively assess the projected cost of hydrogen produced by advanced configuration bio-derived liquids reformer systems. To achieve this objective, several bio-derived liquids (ethanol and glucose) reformation system configurations are defined and evaluated for expected performance and capital cost. Figure 1 displays several general reformation pathways along with the commercial or national lab entity most closely associated with a given approach. Although methane systems were examined for comparison to existing technologies, only steam reforming (ethanol) and liquid phase reforming (glucose) were under consideration in this project. All selected systems were sized to produce 1,500 kg/day of purified hydrogen. While the focus of the work was determination of the capital cost and performance of the

FIGURE 1. Ethanol Reforming Hierarchy

production system, the results were combined with the standard DOE assumptions for hydrogen compression, storage and dispensing to arrive at the total delivered hydrogen cost for comparison with DOE targets.

A baseline ethanol gas-phase reformation system using current technology catalysts and configuration was examined to serve as a benchmark. This baseline system utilizes steam reforming and employs discrete unit reactors (reformation, WGS, pressure swing adsorption [PSA], etc.). Catalyst beds were sized by experimental data and kinetics modeling to the extent possible. System performance was evaluated using HYSYS[®] simulations and system cost was estimated by a combination of scaling factors, previous estimates, and additional Design for Manufacture and Assembly (DFMA[®]) style calculation. The expected total delivered cost of hydrogen was then evaluated using DOE's H2A cost model, which provides a discounted cash flow methodology and standard assumptions regarding hydrogen compression, storage, and dispensing at the forecourt dispensing station.

Advanced technology on-site ethanol reforming systems were also examined. Emphasis was placed on unitized operations to achieve tighter heat integration, smaller reactor volume, enhanced efficiency, and lower capital cost. Integrated reformer/shift beds and integrated reformer/shift/membrane purification beds were examined, and advanced catalysts for lower temperature operation were considered. As with the baseline configuration, the performance was evaluated with HYSYS[®], the capital costs by a variety of methods, and the total hydrogen cost by the H2A model.

A low temperature (225°C) aqueous phase reformer system utilizing glucose as the bio-derived liquid feedstock was also examined. Reactor size was based on published data and projections from Virent Energy Systems, a manufacturer of aqueous phase reformer systems. Capital costs and system performance were estimated using the same methods as described above for gaseous phase ethanol reformers. The H2A model was used to obtain estimated delivered hydrogen cost for the

¹ A process modeling software package from Aspen Technology, Inc.

total dispensing station. Two aqueous reformer cases were analyzed: a current-performance case representing the state of the technology as presented in the published literature and a future-performance case representing specifically-quantified improvements in technology, efficiency and achievement of the DOE 2017 cost target for bio-liquid fuel (\$0.14/kg glucose).

Results

We defined and modeled 21 different systems with a variety of different components, and numerous permutations and combinations of those components. Complete DFMA[®] analyses were conducted on most of these systems, replete with appropriate sizing parameters and material specifications.

The baseline ethanol configuration (see Figure 2) utilizes a two-step reforming approach where the ethanol is converted to methane in a pre-reformer and subsequently is converted to a hydrogen-rich gas using conventional high-temperature (~900°C) steam methane reformer catalysts. A WGS bed followed by PSA is used for CO shift and hydrogen purification, respectively. The baseline unit employs discrete unit reactors (reformation, WGS, PSA, etc.). Conventional tube-and-shell geometry was initially specified for each component, but careful analysis showed that an annular heat exchange reactor geometry was preferable in all cases.

Advanced ethanol reformer configurations considered included one or more of the following elements:

- Medium temperature catalyst: catalyst based on data from Ohio State University (non-precious metals) and the Pacific Northwest National Laboratory (precious metals) that have high conversion at ~500°C.
- Pd-based hydrogen separators instead of PSA units.
- Integrated membrane reformers (where a separation membrane is used to preferentially remove hydrogen

to drive the reforming and/or WGS reactions to a new equilibrium).

- Heat exchange reactor configuration instead of conventional tubular layout.
- Advanced catalyst systems able to avoid coking at low steam to ethanol ratios.
- Advanced PSA systems than can achieve high H₂ recovery (85%) on ethanol reformers while still maintaining five-nines H₂ gas purity (at 300 psi operating pressure).

Table 2 summarizes the configuration and cost results for the main systems of interest. Overall, we note that there is a surprising convergence of performance and cost with three different technology approaches expected to achieve nearly identical performance (68% efficiency and ~\$3/kg H₂ cost): high-temperature reformer with PSA separation, medium-temperature reformer with PSA separation, and medium-temperature integrated (reformer, membrane) systems. We also note that for the “future performance” systems – advanced PSA systems and advanced integrated reactors – there is also a surprising convergence of performance and cost: 75-80% lower heating value (LHV) efficiency and \$2.67/kgH₂. This suggests there are multiple pathways to lower system cost and that no single configuration is clearly favored.

Table 2 also reports the cost results for the aqueous glucose reformer systems. A substantial efficiency and H₂ cost gap is observed to exist between current performance and future performance systems. Efficiency is low primarily due to the currently low hydrogen yield: due to an undesirable side reaction which produces alkanes, only 45% of theoretical amount of hydrogen is currently produced in the reactor. The low hydrogen production efficiency results in high feedstock cost. Additionally, high catalyst loading, and low reactor space velocity results in a high catalyst cost for the current performance aqueous reformer. Projected improvement in efficiency and reduction in hydrogen cost for the future performance system stem from four main assumptions:

- Improvement in catalyst activity (weight hourly space velocity increase from 1/hour to 10/hour).
- Reduction in catalyst loading (from 5% wt to 1% wt Pt loading).
- Improvement in hydrogen selectivity (from 45% to 75% H₂ yield).
- Reduction in feedstock cost (from \$0.23/kg to \$0.14/kg glucose).

Results indicate that the current performance aqueous reformer system results in a very expensive production cost for renewable hydrogen (\$8.28/kgH₂) but achievement of the expected parameter improvements will allow future hydrogen costs of \$2.10/kgH₂.

FIGURE 2. Baseline Configuration Diagram

TABLE 2. Configuration Results

Case #	Description	Feedstock Efficiency (H ₂ LHV/ Feedstock LHV)	Uninstalled Cap. Cost \$	Production Cost \$/kg	Total Cost (Production/ Storage/Disp.) \$/kg
Baseline Ethanol Systems (High Temperature, Pre-Reformer)					
6	- with PSA (75% H ₂ Recovery)	68.1%	\$830k	\$3.01/kg	\$5.03
11	- with Membrane Separator (90% H ₂ Recovery)	74.9%	\$859k	\$2.92/kg	\$4.94/kg
Medium Temperature Ethanol Systems (Steam/EtOH = 8 (PM) /10 (NPM) unless otherwise specified)					
PM = Precious Metal Catalyst NPM = Non-Precious Metal Catalyst					
9	- with PSA (75% H ₂ Recovery)	67.3% (NPM)	\$682k	\$2.97/kg	\$4.99/kg
15		67.5% (PM)	\$891k	\$3.06/kg	\$5.08/kg
9b	- with Future PSA (85% H ₂ Recovery & Steam/EtOH = 4)	75% (NPM)	\$641k	\$2.68/kg	\$4.70/kg
10	- with Membr. Sep. (90% H ₂ Recovery)	64.5% (NPM)	\$567k	\$3.16/kg	\$5.18/kg
17		66.8% (PM)	\$905k	\$3.25/kg	\$5.27/kg
13a	- with Integrated Reformer/ WGS/Membrane System	69.8% (NPM) (Steam/EtOH = 8)	\$711k (\$10/kg catalyst)	\$3.02/kg	\$5.04/kg
13d		67.6% (PM)	\$929k (\$400/kg catalyst)	\$3.23/kg	\$5.25/kg
13b	- Future Integrated Reformer/ WGS/Membrane System	79.4% (NPM) (Steam/EtOH = 6)	\$608k (\$10/kg catalyst)	\$2.67/kg	\$4.69/kg
Aqueous Phase Glucose Systems (Precious metal catalyst)					
16a	- Current Performance Sys.	28.6%	\$1.9M	\$8.28/kg	\$10.30/kg
16b	- Future Performance Sys.	52.6%	\$500k	\$2.10/kg	\$4.12/kg

Conclusions and Future Directions

Key conclusions include:

- Medium and high temperature ethanol reformers have comparable efficiency.
- Alternative configurations to tubular designs may lower capital cost but must have adequate heat transfer to support the endothermic steam reforming reaction.
- Low steam-to-ethanol ratios promote high system efficiency but must not allow coking of the reactor.
- Methane in reformer product gas should be minimized:
 - Each CH₄ molecule in reformer exhaust robs four H₂ molecules from the product.
 - “Methane make” is a key catalyst evaluation metric.
- Catalyst cost is a key cost component. It is worthwhile to explore reduced/non precious metal catalysts but they must have multi-year lifetimes.
- Achieving 90% H₂ recovery in a membrane separator is feasible (at 20 atm reformat/1 atm permeate).
- Membrane systems (with ~90% H₂ recovery) can make significant efficiency improvements (up to 5%) over conventional PSA-based systems (at 75% H₂ recovery).
- Ethanol efficiencies (LHV) in the mid 70% are possible with multiple configurations.
- H₂ Production-only cost of <\$3/kg is feasible with advanced designs.
- Forecourt compression/storage/dispensing is currently very costly and adds ~\$2/kgH₂ to the total hydrogen cost.
 - DOE targets for compression/storage/dispensing need to be met to achieve the overall H₂ cost target of <\$3/kg.
- Integrated reformers have the advantages of:
 - reduced operating temperature
 - lower capital cost
 - lower H₂ \$/kg
- While the cost and efficiency advantage of integrated reformers may not be decisive, integrated systems are compact and simpler: attributes very important for forecourt installations.
- The system that produces the lowest cost hydrogen is an integrated membrane reformer than can successfully utilize a non-precious metal catalyst at low steam-to-ethanol ratios. Development of such a system should be a DOE research goal.
- Aqueous phase reformers are of interest due to their potential for:

- Operation at low temperature.
 - Low capital cost (due to the low temperature and potential for small size).
 - Use of a variety of low cost, renewable feedstocks.
- However, current performance aqueous phase reformers using renewable feedstocks such as glucose result in comparatively high hydrogen cost due to:
 - Currently low hydrogen yield and resulting low H₂ energy conversion efficiency.
 - High precious metal catalyst loading.
 - Low reactor space velocity.
 - Relatively high feedstock cost.
- Future performance aqueous phase reformer systems are expected to improve upon of these deficiencies and when combined with achievement of the DOE 2017 bioliquids cost targets, offer hydrogen costs <\$3/kg.
- Feedstock price was found to be the largest contributor to H₂ cost.

FY 2009 Publications/Presentations

1. “Cost Analysis of Distributed Bio-Derived Liquid Reforming Systems for Hydrogen Production”, Directed Technologies Inc., Project Final Report.

II.B.1 Indirectly Heated Gasification of Biomass to Produce Hydrogen

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used in an updated ASPEN material and energy balance simulation of an integrated biomass to hydrogen process. Yield and capital and operating cost estimates resulting from the simulation were used to update the H2A model for the process. This project addresses the following DOE technical targets outlined in Table 3.1.8 of the HFCIT Multi-Year RD&D Plan:

Technical Targets: Biomass Gasification/Pyrolysis Hydrogen Production

Characteristics	2012 Target	2017 Target
Hydrogen Cost (Plant Gate) (\$2005)	\$1.60	\$1.10
Total Capital Investment (\$2005)	\$150M	\$110M
Energy Efficiency (LHV)	43%	60%

LHV - lower heating value

Objectives

Verify the technical and economic performance of an integrated biomass steam gasification-based hydrogen production process that includes steam gasification, tar and light hydrocarbon reforming, hydrogen sulfide removal, shift reaction, and hydrogen separation.

- Parametric gasification of two biomass feedstocks.
- Gas cleanliness verification with slip stream hydrogen sulfide removal and high temperature shift.
- Update of gas yield correlations.
- Update of ASPEN process simulation model.
- Update of H2A technoeconomic model.

Technical Barriers

This project addresses the following technical barriers from the Production section (3.1.4) of the Hydrogen, Fuel Cells and Infrastructure Technologies (HFCIT) Program Multi-Year Research, Development and Demonstration (RD&D) Plan:

- (T) Capital Cost and Efficiency of Biomass Gasification/Pyrolysis Technology
 - t. Indirect steam gasification efficiency
 - u. Capital cost
 - v. Tar/light hydrocarbon reforming

Technical Targets

This project is directed at the verification of the technical and economic performance of a hydrogen production process using integrated biomass steam gasification. The project experimentally developed gasification data that were used to develop updated gasifier yield and quality estimates. These estimates were

Accomplishments

- Completed parametric steam gasification testing and data reduction and analysis for pine feed:
 - Three temperatures: 750°C, 850°C, 950°C
 - Three steam/biomass ratios: 0.75, 1.25, 2
- Completed multivariate analysis and updated gasifier yield correlations.
- Transferred gasifier correlations to ASPEN.
- Updated the existing H2A model.

Introduction

Through the auspices of DOE's HFCIT Program and based on DOE supported gasification research [1], NREL developed gasifier yield correlations for indirectly heated steam gasification of biomass. These results were used by NREL [2] and others [3] to indicate the feasibility of producing hydrogen and other fuels from biomass. These studies also showed the benefits of catalytically converting high-molecular weight contaminants (tars) and light hydrocarbons (e.g., methane, ethane) in one unit operation. These early efforts were used by NREL to develop detailed ASPEN models and associated economic models [4] that in turn were used to provide yield, capital cost, and operating cost data for use in H2A.

These models and analyses indicate that hydrogen production from biomass may be a viable production pathway. Costs developed in the technoeconomic modeling effort resulted in estimated hydrogen costs of \$1.77/kg (current) and \$1.52/kg (advanced in 2015).

While these estimates are encouraging, they are based on non-integrated pilot scale data generated by Battelle Columbus Laboratories (BCL) in the 1980s. To give additional credibility to the estimates, additional independent verification testing was required. This project provided:

- Experimental data needed to update gasification yields and gas compositions using the NREL pilot development gasification system.
- Data on contaminants and effectiveness of removal.
- Updated H2A analysis for Program evaluation.

Approach

The NREL 150 kWt (maximum of 30 kg/h biomass throughput) thermochemical pilot development unit (TCPDU), Figure 1, was operated to investigate integrated gasification-hydrogen production to generate a raw syngas using a two-stage gasifier (fluid bed and entrained flow thermal cracker), which is cleaned a) using cyclones for particulate matter and an organic quench for tars, water and ammonia; and b) using cyclones, a fluid bed tar reformer, and an organic quench. During operations with the tar reformer, production of a hydrogen-rich syngas in a

micro-scale pressurized catalytic reactor system under high temperature shift conditions was also evaluated. A molecular beam mass-spectrometer system was used to quantify benzene and tars in the syngas before and after the quench. Permanent gases and sulfur compounds (H_2S and COS) were quantified using gas chromatography and non-dispersive infrared analyses. In combination with experimental material balances, updated correlations of gas yield and quality were developed and new ASPEN simulations performed. Economic analyses using H2A protocols were used to compare results with published information.

Results

The project is divided into three tasks:

1) experimental testing, 2) development of gasifier correlations, and 3) updating of ASPEN model and incorporation into an H2A model. The results section discusses these three tasks.

Task 1: Experimental Testing

In general, a higher steam-to-biomass ratio and a higher thermal cracker temperature yielded a higher hydrogen concentration. The hydrogen concentration

FIGURE 1. NREL Thermochemical Pilot Development Unit

ranged from 26–39% vol (dry, N₂-free) for oak and 35–42% vol for pine gasification. The carbon monoxide concentration ranged from 18–31% vol for oak and 15–23% vol for pine. The H₂/CO ratio for oak varied between 0.9 and 2.1 with an average of 1.2. The H₂/CO ratio for pine varied between 1.5 and 2.7 with an average of 2.0. Overall mass closures of 88–100% during the parametric oak gasification studies and 86–100% during the pine gasification studies were achieved. Qualitative tar measurements were very similar between the two feedstocks.

Shift catalyst tests were first performed using bottled gases with an H₂:CO ratio of 4.2, which is representative of the syngas produced in the TCPDU when the tar reformer is online. A CO conversion of 74% was obtained using a shift reaction temperature of 450°C (842°F), steam-to-H₂ ratio of 5.0, and a gas hourly space velocity of 21,000 h⁻¹. The H₂:CO ratio increased from 4.2 at the inlet to 17 at the outlet. The TCPDU was then used to generate pine-derived syngas at a steam-to-biomass ratio of 2.0 and a thermal cracker temperature of 850°C. Using the same shift reactor conditions as in the bottled gas test, the CO conversion using pine-derived syngas was initially 68%. After 6 hours, the CO conversion decreased to 65%. The H₂:CO ratio increased from 4.2 at the inlet to 14 at the outlet. The change in H₂:CO ratio is shown graphically in Figure 2.

Task 2: Gasifier Correlations

The NREL gasification tests examined the effects of several process variables on the gasifier product yields and compositions (e.g., char production rate, tar rates,

FIGURE 2. H₂:CO Ratios During High Temperature Shift Experiments, Gasification of Pine

and dry gas composition) using oak and pine, plus separate data for wheat straw, Vermont wood, and corn stover.

The data collected during the NREL gasification tests were subjected to a regression analysis using Unscrambler statistical software. The significance of several process variables was first tested. The process variables considered were: 1) proximate analysis, 2) ultimate analysis, 3) ash composition (base ratio, dolomite ratio, Ca content), 4) fluid bed temperature, 5) secondary entrained-flow thermal cracker temperature, 6) steam-to-biomass ratio, and 7) residence time.

The significance testing resulted in 18 significant process variables: five ultimate analysis terms (5), four proximate analysis terms (9), gasification temperature (10), steam to biomass ratio (11), residence time (12), three interactions terms (15), and three squared terms (18). Each output variable was modeled by an equation of the form:

$$Y = a + \sum (b \cdot X + c \cdot X^2), \text{ where}$$

Y = Component Value, [=] mole %, kg/kg feed, or mg/Nm³;
X = Independent Variable

Task 3: Updating of ASPEN Model and Incorporation into H2A

In the model, wood is gasified using an indirectly-heated, entrained-flow gasifier. Indirect heat is supplied by adding hot olivine to the gasifier. After gasification, olivine and char are separated from the syngas using cyclones. The char, mixed with olivine, is then combusted to add heat to the olivine, which is then re-circulated back to the gasifier. Steam is also added to the gasifier to aid in stabilizing the entrained flow of biomass and olivine. The syngas exiting the gasifier then passes through a catalytic tar reformer where hydrocarbons and tars are cracked and reformed with water to increase CO and H₂ yields. The syngas is then cleaned of CO₂ and H₂S. The cleaned syngas then passes through two shift reactors that increase the H₂ to CO ratio. Pressure swing absorption (PSA) is then used to separate hydrogen from the syngas.

The feedstock used for the model is hybrid poplar wood chips delivered at 50 wt% moisture. The capacity of the model is 2,000 bone dry tonnes/day. The model requires a small amount of natural gas, although more will probably be necessary for startup. The majority of steam and electricity necessary to operate the envisioned facility is produced by combusting byproducts.

The 2005 Biomass to Hydrogen Design Report [4] presents a techno-economic analysis for two design cases: a current design case and a goal design case. The current design case assumes tar conversion rates verified experimentally with no regeneration of the tar

reforming catalyst. The current design case also includes a steam-methane reformer, prior to the shift reactors, to convert methane and hydrocarbons to CO and H₂. However, the goal design case assumes higher (goal) tar conversion and includes a tar and methane reforming, catalyst regenerating reactor. As such, the goal design case does not include a steam-methane reformer because conversion of methane and hydrocarbons in the tar reformer is high enough that a steam-methane reformer is not justified.

The new correlations replace the old correlations in the Aspen Plus model presented in the Biomass to Hydrogen Design Report [4]. The new correlations predict a slightly different dry gas composition, although the most significant difference is less char. The new correlations predict 0.10 lb of char per lb of dry feed,

whereas the old correlations predict 0.22 lb of char; consequently, a portion of the raw syngas must be diverted to the char combustor to provide the heat necessary for gasification and drying the incoming biomass. The model predicts 2.6% more final hydrogen product when the new gasifier correlations are used (see Table 1).

HFCIT uses a separate economic evaluation spreadsheet, called H2A, available on the DOE H2A Analysis Web site.

The H2A analysis resulted in a hydrogen cost of \$1.56 per kg in 2005 dollars, using the new correlations, versus \$1.52 using the old correlations. The major process and cost data used in the H2A analysis are summarized in Table 2.

TABLE 1. Coefficients of Determination, BCL and NREL Gasifier Data

Component	New Correlation R ²	Old Correlation R ²	New Correlation R ² _{adj}
Hydrogen	0.81	0.92	0.77
Carbon Monoxide	0.64	0.40	0.59
Carbon Dioxide	0.77	0.42	0.73
Methane	0.81	0.70	0.77
Ethane	0.71	0.85	0.52
Ethylene	0.87	0.88	0.85
Acetylene	0.94	0.72	0.93
Propane	0.90		0.88
Propene	0.92		0.90
1-Butene	0.83		0.82
2-c-Butene	0.73		0.68
Hydrogen Sulfide	0.86		0.82
Benzene	0.93		0.92
Toluene	0.72		0.69
Phenol	0.91		0.89
Cresols	0.89		0.87
Naphthalene	0.92		0.89
Phenanthrene	0.85		0.82
Heavy Tar, MW > 180	0.68		0.65
Total Tar, MW > 78	0.82	0.89	0.79
Char	0.78	0.66	0.72
Nitrogen Free Dry Gas Yield	0.87	0.94	0.85

TABLE 2. Comparison of Existing and New H₂A Correlations

	BCL Gasifier	NREL Gasifier
Biomass Usage, kg dry biomass per kg H ₂	11.99	11.68
Electricity Usage, kWh per kg H ₂	1.48	0.95
Natural Gas Usage, Nm ³ per kg H ₂	0.38	0.63
Cooling Water Usage, gal per kg H ₂	2.37	2.46
Process Water Usage, gal per kg H ₂	1.60	2.23
Total Capital Costs, 2005 Dollars	\$155.3 million	\$156.0 million
Annual Fixed Operating Costs, 2005 Dollars	\$10.1 million	\$10.2 million
Annual Variable Operating Costs, 2005 Dollars	\$43.7 million	\$47.5 million
Selling Price, 2005 Dollars per kg H ₂	\$1.52	\$1.56

Conclusions and Future Direction

- A parametric gasification test campaign was completed using the NREL 150 kWt TCPDU, investigating the effects of temperature and steam-to-biomass ratio on yields and gas composition. During the test a new feed (pine) and temperature range (up to 950°C) were used.
- The data from the Fiscal Year 2008 oak test campaign and the 2009 pine test campaign, plus data generated by NREL for the DOE Biomass Program for wheat straw, Vermont mixed wood, and corn stover, were analyzed by multivariate analysis using Unscrambler. Eighteen variables were determined to be significant, including feed ultimate analysis, thermal cracker temperature, steam-to-biomass ratio, and residence time.
- Slip stream high temperature shift experiments were performed using TCPDU product gas. Carbon monoxide conversions comparable to reported results for commercial systems were obtained.
- The results of the regression analysis were incorporated into an existing ASPEN simulation. The simulation model was optimized and capital and operating costs updated.
- The ASPEN model yields, capital costs, and operating costs were used to update the existing H₂A model for a \$60/ton feed. The H₂A analysis resulted in a hydrogen cost of \$1.56 per kg in 2005 dollars, using the new correlations, versus \$1.52 using the old correlations. The conclusion reached was that although the NREL gasifier correlation gave different gas yield because of lower char yield, the integrated process heat requirements and

downstream unit operations (tar reformer, shift reactors, hydrogen separation) resulted in overall process yields and hydrogen costs, thus verifying the earlier results.

Additional modeling work is planned to be completed in Calendar Year 2009 evaluating the feasibility of using PSA tail gas to improve the performance of a sulfur getter that would be located before the tar reformer.

FY 2009 Publications/Presentations

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II.B.2 A Novel Slurry-Based Biomass Reforming Process

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Contract Number: DE-FG36-05GO15042

Subcontractor:

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Project Start Date: May 2, 2005
Project End Date: August 31, 2010

Technical Targets

This project consists of three key elements: plant and system design, catalyst research, and a proof-of-concept demonstration. The information obtained from all three efforts will be used to demonstrate that the proposed H₂ production system will meet the DOE's 2012 Biomass Gasification/Pyrolysis Hydrogen Production energy efficiency and total hydrogen cost targets of 43% (based on feedstock LHV) and \$1.60/kg H₂. The current progress toward achieving the DOE's technical targets based on the preliminary plant and system design is shown in Table 1.

TABLE 1. Technical progress for the project as measured against the DOE's technical targets for biomass gasification/pyrolysis hydrogen production.

Characteristics	Units	2012 Target	Current Status	2008 Status
Hydrogen Cost (Plant Gate)	\$/gge	1.60	1.27 (0.95–1.85)	1.58–2.16
Total Capital Investment	\$M	150	177 (71–365)	203–291
Energy Efficiency	%	43	53.9 (53.9–58)	46.6

Objectives

- Develop an initial reactor and system design, with cost projections, for a biomass slurry hydrolysis and reforming process for H₂ production.
- Develop a cost-effective catalyst for liquid phase reforming of biomass hydrolysis-derived oxygenates.
- Perform a proof-of-concept demonstration of a micro-scale pilot system based on liquid-phase reforming of biomass hydrolysis-derived oxygenates.
- Demonstrate that the proposed H₂ production system will meet the 2012 efficiency and cost targets of 43% lower heating value (LHV) and \$1.60/kg H₂.

Technical Barriers

This project addresses the following technical barrier from the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan [1]:

- (T) Capital Cost and Efficiency of Biomass Gasification/Pyrolysis Technology

Accomplishments

- A baseline 2,000 ton/day biomass to hydrogen plant has been designed using the process simulator HYSYS which has a plant hydrogen efficiency of 53.9%.
- The preliminary economic analysis of the baseline plant design shows that a hydrogen production cost of \$1.27/kg H₂ could be attainable.
- Simultaneous base hydrolysis in the presence of a Pt-Re/CeZrO₂ catalyst results in the complete conversion of yellow poplar sawdust to H₂, CH₄, and C₂H₆ with trace C₃H₈ as well as CO₂.
- The resulting clear, colorless aqueous solutions apparently contained potassium carbonates and possibly trace potassium acetate.

Introduction

This project is focused on developing a catalytic means of producing hydrogen from raw, ground biomass, such as fast growing poplar trees, willow trees, or switch grass. The use of a renewable, biomass feedstock with minimal processing can enable a carbon

neutral means of producing hydrogen in that the carbon dioxide produced from the process can be used in the environment to produce additional biomass. For economically viable production of hydrogen, the biomass is hydrolyzed and then reformed without any additional purification steps. Any unreacted biomass and other byproduct streams are burned to provide process energy. Thus, the development of a catalyst that can operate in the demanding pH, high pressures, and presence of potential poisons is vital to this approach.

Approach

The concept for this project is shown in Figure 1. The initial feed is assumed to be a >5 wt% slurry of ground poplar wood in dilute base. Potassium carbonate, derived from wood ash, is an effective base. Base hydrolysis of the wood is carried out at high but sub-critical pressures and temperatures in the presence of a high surface area, high metal dispersion, large pore, base stable Pt-Re/Ce_(1-x)Zr_xO₂ catalyst. A palladium alloy membrane allows the continuous removal of pure hydrogen, thus limiting methane formation, while the retentate is used as fuel in the proposed plant.

Results

Task 1: Reactor and H₂ Production System Modeling, Energy, and Economic Analysis

The baseline techno-economic analysis was updated to reflect the use of base instead of acid for the hydrolysis process. The model feedstock representing the wood was adjusted to be 72.6% cellulose, 27% lignin surrogate (C₈H₈O₃) and 0.4% ash. The hydrolysis was reduced to a single step process where the alkali is derived from potassium in the wood and where the lignin is completely hydrolyzed. The sulfur removal process was eliminated from the system. The burner system was also adjusted to reflect the combustion of process derived gases, such as methane, rather than unconverted lignin as the experimental work has shown that essentially 100% of the wood can be converted into gas products. The reformer size was also reduced based on the kinetic results from ethanol experiments described later in this report.

FIGURE 1. The UTRC Approach to Biomass Slurry Reforming

FIGURE 2. Reaction product liquor from hydrolysis and liquid phase reforming of 1 wt% yellow poplar at 310°C in 0.1M K₂CO₃ with a 0.5 L/min N₂ sweep gas. White sediment is potassium titanate, a titanium corrosion product.

Task 2: Catalyst Development and Testing

Nearly 100% conversion of 1 wt% yellow poplar was achieved with a Pt-Re/Ce_(1-x)Zr_xO₂ based catalyst in a custom built titanium reactor. Approximately 75% selectivity towards H₂ was achieved with an energy recovery of 75% based on the LHV of yellow poplar. The reaction product liquor is shown in Figure 2. Unfortunately, some corrosion products were evident in the reactor in the form of potassium titanate. The probable major source of this was caustic attack on the titanium screen used to hold the catalyst.

To avoid reactor corrosion and to simplify kinetic studies, it was decided to move to a corrosion resistant flow reactor. A flow reactor was constructed of zirconium. A high pressure Isco syringe pump (500D) is used to pump high pressure reactants. In addition to the liquid reactants, the system is also set up to allow for inlet flows of H₂ and N₂. A high pressure N₂ sweep gas is introduced after the reactor to minimize residence time in the exit piping and act as a diluent for gas production calculation. Upon depressurization to atmospheric pressure, the effluent passes through a gas-liquid separator, followed by a

flow meter and gas chromatographs for analysis. The powdered catalyst is set in the hottest portion of the heated zone, mixed with yttria-stabilized ZrO_2 beads which act as a diluent. The remainder of the reactor is filled with the inert beads.

The initial test of the reactor consisted of using 1 g $\text{Pt-Re/Ce}_{(1-x)}\text{Zr}_x\text{O}_2$ with 1 wt% ethanol as the feedstock. The reactor was operated at temperatures of 250°C, 280°C, and 310°C at a pressure of 1,640 psi with a reactant liquid flow rate of 1 mL/min and a N_2 sweep gas flow rate of 0.3 L/min. At each temperature, the effluent molar flow rates were stable, and increased with increasing temperature. The conversion increased with increasing temperature, with a calculated activation energy for the net formation of H_2 of 54 kJ/mol. The reaction selectivity towards H_2 was 48%, 46%, and 48% at each subsequent temperature step, with CH_4 , and to a lesser degree C_2H_6 , being the main byproducts of the reaction.

Subsequent experiments in the flow reactor were performed with 1.7 wt% ethanol in 0.1M K_2CO_3 to determine how the system behaves in the presence of base. The reactor was run at 250°C, 280°C, and 310°C with a liquid feed flow rate of 2 mL/min, and 3 mL/min, given in Figure 3. For both flow rates, the reaction gas production increased with increasing temperature. Both flow rates produced H_2 as the main product with CH_4 being the major byproduct. CO_2 was only noted at higher temperatures due to the CO_2 scrubbing effect K_2CO_3 will have on the system. More than a saturation level of CO_2 must be generated before any CO_2 will be observed in the gas phase. The H_2 selectivity of the system varied depending on the temperature. The selectivities were 46%, 48%, and 65% at 2 mL/min and 41%, 51%, and 71% at 3 mL/min for 250°C, 280°C, and 310°C, respectively. At 3 mL/min, the reactor was allowed to run for over 200 minutes at

FIGURE 3. Effluent molar flow rate of gas during the liquid phase reforming of 1.7 wt% ethanol in 0.1 M K_2CO_3 with 1 g 1.5% Pt-1.2% $\text{Re/Ce}_{0.65}\text{Zr}_{0.35}\text{O}_2$, at a feed flow rate of 3 mL/min and a sweep gas flow rate of 0.3 L/min at 1,640 psi.

310°C to determine the effect of time on stream. Little degradation in H_2 production was noted during the experiment (the large dip in H_2 production was due to the reactor being taken off line for refilling of the syringe pump). Upon dissecting the reactor after the reactions, it was found that the inert packing had lost its structural integrity and became a powder. More importantly, the beads used as a diluent for the catalyst also lost their integrity, encapsulating the catalyst particles as if in a cement plug. This may have been detrimental to the reaction kinetics of the system and prevented high conversions.

With the data obtained from the liquid phase reforming of ethanol in the presence of base, a network of reactions to describe the system was derived. In addition to the main reaction products of H_2 and CO_2 , only CH_4 , C_2H_6 , and C_3H_8 byproducts were detected in any appreciable quantities. This reaction network led to the development of rate equations and a kinetic model for a plug flow reactor used to estimate the rate constants. Parameter estimation techniques were used to fit the ethanol data to the model. Figure 4 shows the model prediction and experimental data points for the liquid phase reforming of ethanol in 0.1M K_2CO_3 at 310°C. It is evident that the reaction network adequately described the reforming of ethanol at the conditions studied. It is thus possible to use this network to determine optimal conditions and required bed length for high conversion. The approach should also be applicable to more complicated systems, including the liquid phase reforming of raw biomass.

Attempts to run hydrolyzed biomass proved much more difficult than ethanol. Two factors thwarted our efforts: (1) the instability and apparent oligomerization of base-hydrolyzed wood suspensions and (2) the degradation of the inert packing confounding the reactor

FIGURE 4. Model prediction and experimental data for the liquid phase reforming of ethanol at 310°C in 0.1M K_2CO_3 as a function of residence time (tau) in the flow reactor.

liquid flow and catalyst contacting. Support stability studies were conducted at 310°C for 12 hours carried out in a batch high pressure bomb to determine whether acceptable inert materials could be identified. Rutile TiO_2 , Ce stabilized ZrO_2 , and SiC showed promise.

Rutile TiO_2 was used as the next inert packing due to its availability. Yellow poplar (1 wt%) was hydrolyzed in the zirconium autoclave in 0.2 M KOH at 310°C for 10 hours. The hydrolyzed solution was filtered to remove residual solids (approximately 1.2% solids recovered from the original solid loading). After hydrolysis and filtration, it was noted that a solution left out at ambient conditions or in a refrigerator continued to precipitate solids. This discovery may be extremely important in the process, as these tar-like solids may be much more difficult to deal with than the precursors which led to their formation. These precursors are likely highly active lignin fragments that may be best reformed immediately following their production. The solution of hydrolyzed yellow poplar was flowed over a 2 g bed of Pt-Re/Ce_(1-x)Zr_xO₂ chunks (≈4 mm square) mixed with crushed rutile TiO_2 pellets. The total bed volume was 4 cm³. The flow of yellow poplar slurry was set at 1 mL/min and the reactions carried out at 310°C. Unfortunately, significant chromatography issues arose, due to plugging of downstream valves and lines. Data could not be gathered and extensive system repair and redesign has been required.

Work at the University of North Dakota Energy & Environmental Research Center (UND-EERC) has begun. The main emphasis of their work has been on analysis of reaction liquors. Significant learning was necessary in how to properly prepare reaction samples for analysis to quantify production of organic and aqueous phase hydrolysis products. Initial hydrolysis has shown similar results to those performed at UTRC, with complete liquefaction of 1 wt% DM Poplar. Initial analytical results have led to identification of several organic acids in the aqueous phase. However, non-aqueous products have yet to be identified.

Conclusions and Future Directions

Based on the results from this last year, the best path for success is to produce hydrogen using base hydrolysis of wood, probably in the presence of a catalyst that reacts away the hydrolysis products as they are formed. The focus of the project will move toward: (1) the identification of plausible model compound from base hydrolysis studies; (2) model compound reforming studies in a flow reactor to enable the capture of fundamental reaction engineering information; and (3) system design of a coupled wood hydrolysis/reforming system based on this information. Once this is tested and refined work can proceed toward a hydrogen separation membrane enabled demonstration unit.

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II.B.3 Catalytic Solubilization and Conversion of Lignocellulosic Feedstocks to Hydrogen

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Project Start Date: October 2007
Project End Date: October 2008

Objectives

Develop novel chemical routes and catalysts to produce hydrogen/syngas from lignocellulosic feedstocks.

Technical Barriers

This project addresses the following technical barriers from the Biomass Gasification/Pyrolysis Hydrogen Production section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

(T) Capital Cost and Efficiency of Biomass Gasification/Pyrolysis Technology

- Integration of gasification and aqueous phase reforming using lignocellulosics as a primary feedstock.

Feedstock Cost and Availability. Feedstock costs are high. Improved feedstock/agriculture technology (higher yields per acre, etc.), lower cost feedstock collection, and improved feedstock preparation are needed. Because biomass feedstocks are seasonal in nature, feedstock-flexible processes and cost-effective feedstock storage are needed. (Tasks to overcome these barriers are the responsibility of the DOE Biomass Program and the U.S. Department of Agriculture.)

Capital Cost and Efficiency of Biomass Gasification/Pyrolysis Technology. The capital cost for biomass gasification/pyrolysis needs to be reduced.

Process intensification by combining unit operations can significantly reduce capital costs. This could range from combining the current two step water-gas shift and pressure swing adsorption separation to a one step water-gas shift with integrated separation, to integrating gasification, reforming, water-gas shift and separation all in one unit operation. Improved process efficiency and higher hydrogen yields and selectivities through catalyst research, better heat integration, and alternative gas clean-up approaches are needed. Improved catalysts or engineering approaches for tar cracking are also needed.

Technical Targets

LANL is conducting applied research that will increase the research knowledge base on biomass solubilization/depolymerization and hydrogen producing reaction pathways from biomass. LANL's research is anticipated to provide alternative routes to hydrogen production from biomass that are aimed at meeting or exceeding the DOE targets (Table 1).

TABLE 1. DOE Technical Targets for Hydrogen Production via Biomass Gasification/Pyrolysis

Characteristics	Units	2005 Status	2012 Target	2017 Target
H ₂ Cost (Plant Gate)	\$/gge	<\$2.00	\$1.60	\$1.10
Total Capital Investment	\$M	<\$194	\$150	\$1
Energy Efficiency	%	>35%	>43%	>60%

Accomplishments

- Conversion of cellobiose to glucose is feasible, but rates currently too low.
- Recent results of low-temperature catalyzed pyrolysis of lignin shows potential.
- Demonstrated heterogeneous catalysis of glucose and cellobiose:
 - Relatively high conversions during batch reaction (~60 – 90%).
 - Major products appear to be gas phase for heterogeneous catalysis.
- Demonstrated homogeneous catalysis of cellobiose hydrolysis to glucose without significant decomposition and/or caramelization.
 - Aqueous cellulose suspension marginally hydrolyzed to free glucose.

- Solid conversion of lignin and pine increased by Lewis Acid catalysis.
 - Gas phase products tend to syngas rather than alkanes.
 - Minimal structural change of remaining lignin (thermal gravimetric analysis, nuclear magnetic resonance, diffuse reflectance infrared Fourier transform spectroscopy).
 - Some change in vibrational structure with La Triflate.
 - Lignin/Gd Triflate demonstrates different decomposition mechanism.
- Demonstrated catalytically enhanced decarboxylation of lignin.

Introduction

Aqueous-phase reforming (APR) at low temperature has been successfully demonstrated for simple sugars, sugar alcohols, and glycols. In these instances, the simple sugars are derived from cellulosic feedstocks via acid or base hydrolysis via batch processing followed by neutralization of the sugar solutions to near-neutral pH. Successful approaches to the direct utilization of lignocellulosic feedstocks using APR to convert the carbon-hydrogen bonds of polymeric or oligomeric cellulose into hydrogen directly have not been demonstrated. We propose to seek out direct or tandem routes from lignocellulosic feedstocks to hydrogen, gaining a significant advantage in feedstock cost reduction while maintaining the low pressure, low temperature capital cost advantages of aqueous phase reforming that have been demonstrated by others.

Utilization of lignocellulosic biomass to generate CO_2 -neutral, renewable hydrogen is an attractive pathway to meet the DOE goal of producing hydrogen at a cost of \$2-3/gallon gasoline equivalent. Existing technology based on glucose or sorbitol results in approximately twice the target cost given current estimates. In addition, utilization of more of the biomass by being able to process lignin, which represents up to 30% of many sources of biomass, is anticipated to yield additional hydrogen per unit of biomass. Catalytic approaches to solubilization and depolymerization of lignocellulose also offer the advantage that they eliminate the use of stoichiometric dilute acid or base to hydrolyze the cellulose to sugars, and obviate the need to deal with the large mass of salt that results from eventual neutralization of the acid or base solutions.

Approach

In general terms, LANL is in search of novel hydrogen production routes from lignocellulosics. Two approaches will be explored: 1) catalytic solubilization of cellulose to generate a sugar feedstock stream for downstream APR, and 2) solubilization of lignocellulosics followed by aqueous phase reaction (APR_{xn}) of oligomeric, soluble cellulose.

LANL will conduct screening experiments for evidence of direct aqueous phase reforming of cellulose to hydrogen through the use of catalysts designed to cleave carbon-carbon bonds of the cellulose backbone. Tandem catalysis approaches, where two catalysts or processes are linked together in a single reaction vessel, will be explored to demonstrate “one-pot” cellulose solubilization followed by aqueous phase catalytic reforming to generate hydrogen. This is important in that if catalysts can be found that will generate hydrogen directly from soluble cellulose oligomers, this provides a ‘one-pot’ approach and offers potential for cost reductions both in feedstock and in capital equipment. LANL’s approach to producing hydrogen from lignocellulosics (i.e., middle and bottom routes) is represented by the chemical routes shown in Figure 1.

Results: Hydrolysis of Cellobiose to Glucose

For a complete summary of our research, please refer to our 2009 DOE Annual Merit Review presentation (project ID: pdp_12_semelsberger). LANL has investigated catalytic routes of glucose production (which then can be reformed to bio-syngas) from cellobiose (i.e., oligomers of glucose). Depicted in Figure 2 is the reaction of cellobiose to glucose reaction that is being investigated.

FIGURE 1. A Rudimentary Diagram Showing LANL’s Approach to Producing Bio-Syngas (i.e, Hydrogen and Carbon Monoxide) from Lignocellulosics

LANL has demonstrated the feasibility of converting cellobiose to glucose via catalytic hydrolysis routes. Figure 3 shows the nuclear magnetic resonance results of the uncatalyzed thermal treatment of cellobiose and the results of a catalyzed treatment of cellobiose (the carbon color coding correlate to those in Figure 2). The uncatalyzed reaction of cellobiose does produce trace amounts of glucose. In contrast, the catalyzed reaction of cellobiose produces greater quantities of glucose as compared to the control experiment. These results are promising in that the low temperature catalyzed hydrolysis of cellobiose is feasible. Although the results are feasible, the rates are still too low. Further research on improving catalyst performance (i.e., rates) is necessary.

Results: Low-Temperature, Catalytic Pyrolysis of Lignin

Recent LANL results has shown the low-temperature catalytic pyrolysis of lignin (Aldrich). Shown in Figure 4 and Figure 5 are the thermogravimetric analysis-mass spectrometer results of the uncatalyzed and catalyzed pyrolysis of lignin. In the uncatalyzed pyrolysis of lignin, lignin was the only reactant. In the catalyzed reaction, lignin was

physically mixed with a catalyst forming a solid-phase homogeneous mixture. On the industrial scale, the solid-phase catalytic reaction of lignin is not most likely an unviable process, but the primary objective is to uncover the reaction mechanism. Understanding the reaction mechanism allows for catalyst optimization and novel industrial-scale catalytic processes.

The pyrolysis products for both cases (catalyzed and uncatalyzed) are carbon dioxide, methane, and hydrogen. The uncatalyzed pyrolysis of lignin produces hydrogen around 700°C, while the catalyzed pyrolysis of lignin produces hydrogen around 400°C. In both cases, the observed weight loss percentage is the same. The observation of similar weight loss percentages are a coincidence because the added mass of the catalyst is also included in the weight loss percentage. The result of the catalyzed pyrolysis of lignin are encouraging

FIGURE 2. Schematic of Cellobiose to Glucose Reaction

FIGURE 3. Catalyzed Hydrolysis of Cellobiose to Glucose (1 mol % $Gd(OTf)_3$, 0.33 mol cellobiose/L H_2O , 120°C for 13 hrs)

FIGURE 4. Lignin Pyrolysis in the Absence of a Catalyst ($T_{\text{ramp rate}} = 5^\circ\text{C}/\text{min}$, N_2 purge rate = 30 ml/min)

FIGURE 5. Low-Temperature, Catalytic Pyrolysis of Lignin ($T_{\text{ramp rate}} = 5^\circ\text{C}/\text{min}$, N_2 purge rate = 30 ml/min)

because not only is hydrogen produced at a lower temperature, but the selectivity has also changed.

Conclusions

- Conversion of cellobiose to glucose is feasible, but rates currently too low.
- Lignin hydrophobicity is a critical challenge for APRxn processes.
- Recent results of low-temperature catalyzed pyrolysis of lignin shows potential.
 - Mechanism of the low-temperature catalyzed pyrolysis of lignin currently unknown.
- Heterogeneous catalysis of glucose and cellobiose.
 - Relatively high conversions during batch reaction (~60–90%).
 - Major products appear to be gas phase for heterogeneous catalysis.
- Homogeneous catalysis of cellobiose hydrolysis to glucose without significant decomposition and/or caramelization.
 - Aqueous cellulose suspension marginally hydrolyzed to free glucose.
- Solid conversion of lignin and pine increased by Lewis Acid catalysis.
 - Gas phase products tend to syngas rather than alkanes.
 - Minimal structural change of remaining lignin (thermal gravimetric analysis, nuclear magnetic resonance, diffuse reflectance infrared Fourier transform spectroscopy).
 - Some change in vibrational structure with La Triflate.
 - Lignin/Gd Triflate demonstrates different decomposition mechanism.

Future Directions

- Continue screening for novel hydrogen production catalysts.
- Explore conversion chemistry of model monolignols.
 - Develop heterogeneous catalyst for aqueous phase reactions.
- Focus on chemistry and catalyst development for cellulosic conversion.

II.C.1 Zeolite Membrane Reactor for Water-Gas Shift Reaction for Hydrogen Production

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Contract Number: DE-PS36-05GO15043

Subcontractors:

- University of Cincinnati, Cincinnati, OH
- Arizona State University, Tempe, AZ
- Ohio State University, Columbus, OH

Start Date: July 1, 2005

Projected End Date: June 30, 2009

Objectives

- To synthesize chemically and thermally stable silicalite membranes with hydrogen permeance $>5 \times 10^{-7}$ mol/m²·s·Pa and H₂/CO₂ selectivity >50 .
- To fabricate tubular silicalite membranes and membrane reactor module suitable for membrane reactor applications.
- To identify experimental conditions for the water-gas shift (WGS) reaction in the zeolite membrane reactor that will produce a hydrogen stream with at least 94% purity and a CO₂ stream with 97% purity.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section (3.1) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) Reforming Capital Costs for Distributed Hydrogen Production
- (C) Operation and Maintenance Cost of Distributed Hydrogen Production

- (K) Membrane Durability for Hydrogen Separation
- (N) Membrane Hydrogen Selectivity
- (P) Membrane Hydrogen Flux

Technical Targets

This project is focused on fundamental studies of zeolite membrane reactor for water-gas shift reaction for hydrogen production. Insights gained from these studies will be applied towards the development of low cost, high efficiency technology for distributed and central hydrogen production that meets the following DOE 2010 hydrogen storage targets:

- Cost: \$0.4/kg
- Flux rate: 200 scfh/ft²
- Hydrogen recovery: $>80\%$
- Hydrogen quality: 99.5%
- Operating capability: 400 psi
- Durability: 26,280 hrs

Accomplishments

- Improved reproducibility of silicalite seed layers and membranes.
- Improved the performance of chemical vapor deposition (CVD)-modified MFI (a zeolite structure code) zeolite membranes (H₂ permeance: $>1.35 \times 10^{-7}$ mol/m²·s·Pa, H₂/CO₂ separation selectivity: >60).
- Understood fundamentally the mechanism of CVD modification by using methyl-diethoxy silane (MDES) as the silicon source.
- Conducted CVD modification on tubular MFI membranes.
- Conducted WGS reaction in a tubular membrane packed with developed catalyst.
- Developed tubular membrane supports with smoother inner surface by optimizing the dispersion chemistry and deposition of mesoporous intermediate layers on the supports.
- Developed ternary spinel-based catalysts for sulfur-tolerant WGS reaction.

Introduction

Gasification of biomass or heavy feedstocks to produce hydrogen fuel gas using current technology includes partial oxidation to produce syngas, the WGS

reaction to convert carbon monoxide with water to hydrogen, separation of hydrogen from the product stream, and removal of water vapor and other impurities (such as H_2S) from the CO_2 containing stream. Commercially, WGS is normally conducted in two or more reactor stages with inter-cooling to maximize conversion for a given catalyst volume. Complete conversion of WGS is possible in a single membrane reactor at high temperatures ($\sim 400^\circ\text{C}$). The membrane removes product hydrogen from the reactor, facilitating higher conversion at a given temperature.

This project is focused on experimental and theoretical studies of the synthesis of a new hydrogen permselective and thermally/chemically stable zeolite membrane and its use in the membrane reactor for the WGS reaction to produce hydrogen and CO_2 rich streams. The membrane reactor system is designed for operation with feeds containing sulfur or other biomass residual contaminants. The zeolite membrane consists of a continuous thin ($1\text{--}3\ \mu\text{m}$), aluminum-free silicalite film without intercrystalline micropores on a support with macroporous zirconia and mesoporous silicalite intermediate layers. These composite silicalite membranes in disk and tubular geometries were prepared by a unique technique that combines several synthesis methods including a template-free secondary growth step. Research efforts were also directed towards development of the cost-effective microwave method to synthesize the MFI zeolite (silicalite and high Si/Al ratio ZSM-5) membranes in disk and tubular geometries. A new catalyst was developed for the WGS reaction under membrane reactor conditions. The final research task is to perform experimental and modeling studies on the performance of the WGS reaction in the membrane reactors with the silicalite membranes and the catalyst developed in this project. The results obtained in this project will enable development of a large-scale one step membrane reactor process for the WGS reaction for cost-effective production of hydrogen to below $\$0.40/\text{kg}$.

Approach

The approach used in this project is to study fundamental issues related to synthesis of high quality, stable zeolite membranes and a membrane reactor for WGS reaction and hydrogen separation. The details of project are to (1) synthesize disk-shaped and tubular supports with desired intermediate layers and silicalite membranes with a template-free hydrothermal synthesis method, (2) optimize the hydrothermal synthesis condition and perform thorough permeation and separation characterization of silicalite and ZSM-5 membranes, (3) perform CVD for improvement of H_2 permselectivity, (4) develop a microwave synthesis approach to more efficiently and cost-effectively synthesize high quality silicalite membranes, (5) obtain a new WGS catalyst with activity and selectivity

comparable to the best available commercial catalyst with improved chemical stability for SO_2 and H_2S containing WGS reaction stream, and (6) develop methods to fabricate a tubular membrane support with desired intermediate layers and a membrane module and sealing system for a tubular membrane reactor that can be operated in WGS conditions.

Results

The work conducted on zeolite membranes during this reporting period was focused on CVD modification to repair the intercrystalline pores using tetra-ethoxy silane (TEOS) and narrow MFI zeolite pores using MDES to further improve the H_2/CO_2 separation selectivity of MFI zeolite membranes. Investigation of CVD modification mechanism and reproducibility study of zeolite membrane synthesis were also conducted during this year.

MFI zeolite membranes were synthesized by template-free secondary growth of zeolite crystals on silicalite seeded porous supports. High quality and reproducibility silicalite seed layers were obtained by dip-coating of silicalite suspension with optimized concentration on smooth alumina porous supports. Single gas permeation experiments were performed on as-synthesized and CVD modified membranes. After CVD modification, the permselectivity of H_2/CO_2 increased from 0.6 to 44.3 at 297 K, and 4.2 to 146.9 at 673 K. A CVD-modified membrane was tested by separation of H_2/CO_2 (50:50) gas mixtures and the results are shown in Figure 1. After CVD modification with TEOS, the H_2 permeance decreased by $\sim 33\%$ but the H_2/CO_2 selectivity only increased from 3.4 to 5.2 because the large TEOS molecules ($d_k = 0.96\ \text{nm}$) are unable to enter the intracrystalline pores but can access and modify the nanometer-scale intercrystalline pores. After switching the precursor from TEOS to MDES, the H_2/CO_2 selectivity dramatically increased to 22.6 with

FIGURE 1. H_2/CO_2 separation results during the CVD modification of a disk membrane using TEOS and MDES.

only an additional ~5% decrease in H_2 permeance. The results indicate that there was no silica film deposited on the TEOS-modified membrane surface to block the pore entrances for MDES molecules.

CVD modification was also conducted on a tubular zeolite membrane and the results are shown in Figure 2. The surface of the zeolite membrane layer was exposed to MDES at 450°C in the first round of the CVD modification. The separation factor of H_2 to CO_2 increased from 3.0 to 28.5 with the H_2 permeance decreasing from $3.32 \times 10^{-7} \text{ mol/m}^2 \cdot \text{s} \cdot \text{Pa}$ to $1.63 \times 10^{-7} \text{ mol/m}^2 \cdot \text{s} \cdot \text{Pa}$. The membrane was modified for the second round for 8 hours at the same modifying conditions (at 450°C, no pressure difference, with sweeping gas). The separation factor of hydrogen to CO_2 further increased from 28.5 to 60.2 with the H_2 permeance decreased from $1.63 \times 10^{-7} \text{ mol/m}^2 \cdot \text{s} \cdot \text{Pa}$ to $1.35 \times 10^{-7} \text{ mol/m}^2 \cdot \text{s} \cdot \text{Pa}$. Primary experiments have shown that a small amount of H_2S (0.5 mol%) in the feed stock has little effect on the separation performance. No H_2S was detected in the permeate stream indicating a high H_2/H_2S selectivity.

The modification mechanism of MFI membrane with MDES was studied during the past year to gain better understanding of CVD modification process and to optimize the CVD modification procedure. Fourier transform infrared (FTIR) spectroscopy was used to investigate the CVD modification of zeolite sample by MDES and the results are shown in Figure 3. After adsorbing MDES vapor at 423 K, the peaks of $Si-OC_2H_5$ (~2,990 cm^{-1}), $Si-H$ (~2,160 cm^{-1}), and $Si-CH_3$ (~1,405 cm^{-1}) appeared as a result of chemical and physical adsorption of MDES. In the sample treated at 573 K, the peaks of $Si-H$, and $Si-CH_3$ disappeared and the $Si-OC_2H_5$ peak remained strong. When the modification temperature increased to 723 K, the $Si-OC_2H_5$ peak also disappeared with strong silanol peak remaining at ~3,740 cm^{-1} . This result suggests the final deposits are likely to be $(OH)_3Si\{O-Si\}_{\text{framework}}$ in the H_2/CO_2 carrier gas.

FIGURE 2. Separation performance of the tubular membrane after modification (29-37 hr for the first round; 46-54 hr for the second round).

To obtain tubular membrane supports with a smoother inner surface appropriate for zeolite membrane growth, flow coating was performed on tubular supports made from AA3 powder (Sumitomo Chemical Corp.) which have a slightly smaller pore size (approximately 1 μm) and a smoother surface when compared to the Pall tubular $\alpha\text{-Al}_2\text{O}_3$ supports. The chemistry of the AKP30 dispersion was optimized by adjusting the AKP30 solid load, additive content and composition. An additional vacuum treatment step was also performed to remove any microbubbles after mixing of the dispersion to ensure high quality of the AKP30 coating on AA3 supports. This process involved a brief sonification treatment in an ultrasonic bath for approximately 30 sec, followed by evacuation inside of a pressure-controlled vacuum chamber for about 15 min. After drying, the coated tubular supports were fired at 950°C for 3 hrs. To further improve the quality of AKP30-AA3 supports, a $\gamma\text{-Al}_2\text{O}_3$ mesoporous intermediate layer was deposited on AKP30 modified AA3 supports. The $\gamma\text{-Al}_2\text{O}_3$ precursor dispersion was prepared by mixing Boehmite [$AlO(OH)$] sol and 3 wt% polyvinyl. The dip dispersion was screened with 20 μm nylon mesh, sonicated in an ultrasonic bath, and then evacuated for about 20 min to remove microbubbles. The $\gamma\text{-Al}_2\text{O}_3$ coated tubular supports were fired at 600°C for 3 hrs. Scanning electron microscopy observation of the surface and cross-section of the $\gamma\text{-Al}_2\text{O}_3$ deposited AKP30-AA3 supports was performed and compared with the microstructure of AKP30-AA3 supports. The

FIGURE 3. FTIR spectra of MFI zeolite samples: (a) before modification, (b) MDES adsorbed at 423 K, (c) MDES adsorbed at 573 K, and (d) modified by MDES at 723 K.

FIGURE 4. (a) Cross section of a γ -Al₂O₃ membrane on an AKP30-AA3 tubular support; (b) Surface of a γ -Al₂O₃ membrane on an AKP30-AA3 tubular support; (c) Surface of an AKP30 coated AA3 tubular support; (d) γ -Al₂O₃ membrane on the inner surface of an AKP30-AA3 tubular support; (e) Flow coating apparatus.

results shown in Figure 4 indicate that the γ -Al₂O₃ layer results in a surface that is smoother than that of the AKP30-AA3 support and the γ -Al₂O₃ layer appears to be defect-free.

The work on catalysis was focused on optimizing the atomic ratio between Fe to M (M=Ce, Cr). The chosen Fe/M ratios were 10:1, 10:0.5 and 10:2. Ammonia assisted co-precipitation route was explored for high-yield preparations of various modified spinels Fe/M (M = Ce, Cr) at different iron to metal ratio. Iron nitrate, chromium nitrate and cerium nitrate was chosen as precursors. In a typical preparation, the calculated amounts of nitrates were dissolved separately in deionized water and mixed together. Dilute aqueous ammonia was added gradually drop wise to the aforementioned mixture solutions, with vigorous stirring, until precipitation was complete (pH 8.5). The obtained precipitates were filtered off, dried at 80°C for 12 hrs and finally calcined at 500°C for 3 hrs in N₂ environment. The previous results indicated that copper acted as a promoter for the Fe/Cr catalyst,

while it acted as an inhibitor for the Fe/Ce catalyst. To study the role of copper on modified ferrites, copper-doped ferrite-based ternary catalysts Fe/Cu/M (atomic ratio 10:1:0.25) (M=Co, Ni, Mn, Zn, Ce, Cr) were synthesized. The preparation process is similar to that of Fe/M (M=Ce, Cr) as described above except that a portion of the precipitated gels were subjected to ultrasonic treatment for 30 min to improve the textural and thermal stability of the prepared catalysts. The catalytic properties of the synthesized catalysts will be tested and the optimal catalyst WGS reaction will be screened.

Preliminary WGS reaction was performed on the zeolite membrane reactor to test the feasibility of the zeolite membrane reactor for WGS. Figure 5(a) shows experimental setup for the WGS membrane reactor. The membrane was fixed in a stainless steel cell with the silicalite membrane facing opposite to the feed side, and was sealed by graphite rings. The WGS Fe/Cr catalyst described above, with particle size of about 150 μ m, was filled in the chamber in the feed/retentate side (or α -Al₂O₃ side) of the zeolite membrane.

FIGURE 5. (a) Schematic of membrane reactor setup for WGS reaction, (b) CO conversion for WGS reaction under H_2O/CO ratio of 1 and space velocity of $3,500\text{ h}^{-1}$ in the disk-shaped silicalite membrane reactor with Fe/Cr WGS catalyst, fixed-bed reactor, (c) Tubular WGS membrane reactor.

Permeation and reaction experiments were conducted in 573–773 K with a heating/cooling rate of 30 K/h without purging gas in all experiments. The upstream pressure was regulated by a needle valve at the retentate side while keeping the permeate side atmospheric. The flow rates and compositions of the retentate/permeate

were respectively measured or analyzed by bubble flow meters and gas chromatography with a thermal conductivity detector (5973 Agilent gas chromatograph/mass spectrometer system with stainless-steel column; HAYESEP DB [ALLTECH]). Simulated fixed bed reactor was carried out by closing the permeate side and only gas mixtures from the retentate side were analyzed by gas chromatograph.

Figure 5(b) shows the effect of reaction temperature on CO conversion for membrane and simulated fixed-bed reactor with $H_2O/CO=1$ and gas hourly space velocity $= 3,500\text{ h}^{-1}$. CO conversion increases with temperature for both kinds of reactors, which is opposite to the trend of thermodynamic variation. Moreover, CO conversion difference between these two operating reactors increases with the increase of temperature. At 773 K, CO conversion for the membrane reactor reaches 82.5%, which exceeds thermodynamic equilibrium conversion (69.1%). The results clearly show advantages of using the zeolite membrane reactor for WGS reaction. A tubular zeolite membrane reactor, including high temperature seals, has been fabricated, as shown in Figure 5(c). Research next year will be focused on WGS reaction experiments on the tubular silicalite membrane reactor using higher quality silicalite membrane.

Conclusions and Future Directions

Conclusions

- Improved the reproducibility of silicalite seed layers by dip-coating of silicalite suspension with optimized concentration on smooth alumina porous substrates.
- Improved the CVD modification procedure and obtained high H_2/CO_2 separation selectivity (>60) and considerable H_2 permeance ($1.35 \times 10^{-7}\text{ mol/m}^2\cdot\text{s}\cdot\text{Pa}$).
- Investigated fundamentally the CVD modification mechanism when MDES is used as a silicon source.
- Conducted CVD modification on tubular MFI membranes and improved significantly the performance of the modified tubular membranes.
- Conducted WGS reaction in a tubular membrane reactor packed with a catalyst developed in this project.
- Developed tubular membrane supports with high quality inner surface by optimizing the dispersion chemistry and deposition of mesoporous $\gamma\text{-Al}_2\text{O}_3$ intermediate layers on the AKP30 modified supports.
- Developed and optimized ternary spinel-based catalysts for sulfur-tolerant WGS reaction.

Future Work

- Synthesize high quality membranes and optimize the CVD modification procedure to further improve the membrane performance (i.e. with a higher H₂ selectivity and flux).
- Perform the WGS reaction in the CVD-modified MFI tubular membranes, and investigate the performance of the zeolite membrane reactor.
- Modeling the WGS reaction on the silicalite membrane reactor.
- Optimize the dispersion chemistry and improve the deposition of mesoporous intermediate layers on the tubular supports.
- Perform full optimization of the WGS catalysts in conjunction to the WGS membrane reactor, characterize and develop the most effective catalysts.
- Economic evaluation of the project results to validate the scale-up and operation in an industrial scale.

FY 2009 Publications/Presentations

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3. A. Khan and Panagiotis G. Smirniotis, "Contaminant Tolerant Catalysts for High Temperature Membrane WGS Reaction" To be presented at *100th AIChE Annual Meeting*, Philadelphia, PA, Nov 16-21, 2008.
4. Z. Tang, S.-J. Kim, J. Dong, Modification of Internal Surface in MFI-Type Zeolite Membranes for High Selectivity and High Flux Hydrogen Separation. *North American Membrane Society (NAMS) Annual Meeting*, June 20-24, 2009, Charleston, South Carolina USA.
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II.C.2 High Performance Palladium-Based Membrane for Hydrogen Separation and Purification

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Contract Number: DE-FG36-05GO15093

Subcontractors:

- Colorado School of Mines, Golden, CO
- Oak Ridge National Laboratory, Oak Ridge, TN

Project Start Date: July 1, 2005
Project End Date: June 30, 2010

Objectives

- The overall project objective is the development, demonstration and economic analysis of a Pd-alloy membrane that enables the production of 99.99% pure H₂ from reformed natural gas as well as reformed bio-derived liquid fuels (BILF) such as ethanol at a cost of \$2-3/gge by 2010.
- The objectives for the past year were to identify and control the variables that influence the performance, economics and manufacturability of a suitable Pd-alloy membrane; and to demonstrate membrane performance in pure component as well as mixed gas studies.
- Another objective was to assess the cost impact of the membrane on the overall reforming system potentially reducing H₂ production cost by integration of the membrane in the reforming process.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section of the Hydrogen, Fuel Cells and Infrastructure Technologies

Program Multi-Year Research, Development and Demonstration Plan:

- (A) Reformer Capital Costs
- (B) Reformer Manufacturing
- (C) Operation and Maintenance (O&M)
- (E) Greenhouse Gas Emissions
- (K) Durability
- (L) Impurities
- (M) Membrane Defects
- (N) Hydrogen Selectivity
- (O) Operating Temperature
- (P) Flux
- (Q) Testing and analysis
- (R) Cost

TABLE 1. Applicable Technical Targets for Dense Metallic Membranes and Current Project Status

Performance Criteria	2010 Target	2015 Target	Pall Status 2009
Flux SCFH/ft ² @ 20 psi ΔP H ₂ partial pressure and 15 psig permeate side pressure	250	300	270*
Membrane Cost, \$/ft ² (including all module costs)	\$1,000	<\$500	<\$1,000
ΔP Operating Capability, system pressure, psi	400	400 - 600	400
Hydrogen Recovery (% of total gas)	>80	>90	>60**
Hydrogen Permeate Quality	99.99%	>99.99%	99.999%***
Stability/Durability	2 years	>5 years	TBD

*Maximum observed flux. Average flux over more than 20 samples
~190 scfh/ft² Economic analysis indicates separation factor rather than flux
to be stronger determinant of cost of hydrogen production

** Measured on a 50%H₂/21%H₂O/up to 3.5% CO/Balance CO₂ mixed gas
stream. Hydrogen flux and recovery measurements are planned with other
impurities starting in mid-2009. The experimentally observed recovery is
determined by chosen operating conditions and is not necessarily a limit of
the membrane performance.

*** Projected purity based on H₂/N₂ ideal selectivity.
SCFH – standard cubic feet per hour; TBD – to be determined

Accomplishments To-Date with Specific Barriers Addressed

- Increased operating capabilities to 400 psi at 550°C though use of 310SC SS tubular substrate.

- Optimized and scaled up the diffusion barrier coating process to 12" lengths with manufacturing capability of producing up to 1 m length substrate tubes. A commercial welding process has been developed for welding non-porous fittings to porous tube (B, R).
- Developed additional sequential steps in the membrane synthesis process (air oxidation and layering sequences) to improve membrane performance as well as for repairing defects (M, N and P).
- Characterized membrane performance using synthesis gas mixtures (L, Q).
- Determined sulfur tolerance of the Pd-alloy membranes with promising results (K, L, N, P, Q).
- Fabricated, installed, and started up two larger mixed gas test stands to perform sensitivity analyses to water-gas shift (WGS) reaction impurities and long term durability testing, respectively (K, L, N, P, Q).
- Tested membranes at high pressure WGS reaction environment conditions for up to 120 hours. High mixed gas hydrogen flux rate ($145 \text{ scfh/ft}^2\text{-atm}^{0.5}$) and high hydrogen purity ($<99.95\%$) were observed at an operating feed side pressure of $>200 \text{ psig}$ (K, L, N, P, Q).
- Demonstrated membrane performance stability against thermal cycling ($50^\circ - 400^\circ\text{C}$) (K, Q).
- Conducted a preliminary evaluation of the module design, fabrication techniques and materials for a stand-alone membrane separator device that showed that a cost of less than \$1,000 per ft^2 of area to the end user is achievable (A, R).
- Preliminary H₂A modeling analyses by Directed Technologies, Inc. (DTI) determined that the hydrogen flux rate of a membrane and its capital cost exhibited much smaller impact on the cost of hydrogen production when compared to the hydrogen recovery by the membrane (A, C, N, P, R).
- Membrane-based process can enable cost reduction through process intensification and cost analysis by DTI indicated that the hydrogen production cost target of \$3/kg is achievable (A, C, R).

Introduction

This project is focused on optimizing the overall composition of the Pd alloy, intermediate layers and tubular support, as well as the manufacturing methods required to produce a very thin, high-flux, cost effective membrane for H₂ separation and purification on a robust, porous, inorganic substrate. The substrate used is Pall's AccuSep® inorganic media which is readily scalable to high volume production as it is manufactured in long lengths. Robust high-area modules can be

made by welding multiple tubes into a pressure vessel, eliminating low temperature seal materials.

Approach

The approach is to further develop and optimize the performance of Pd alloy membranes that have been shown to have both high flux rate and high separation factor for H₂ from reformat. This is being accomplished by design of a composite membrane based on robust, tubular, porous metal media as a substrate. The substrate is modified by the addition of a uniform, fine pore size diffusion barrier layer. The deposition methods are modified to produce a thin, uniform, functional gas separation Pd-alloy membrane layer. The project plan includes commercial scale up of the high quality porous metal substrate and diffusion barrier layer that enables the development of a technically and economically viable composite membrane. Membrane alloy composition and thickness will be optimized for assuring high hydrogen flux and selectivity as well as long-term durability with tolerance to contaminants. The membrane performance will be determined under operating conditions in a typical reformed natural gas or BILI stream. The H₂A model, modified to incorporate a membrane reactor design, will be used to verify economic viability. Our plan is to confirm an increase in the overall energy efficiency of a H₂ reforming system through the use of membrane technology for process intensification. Economic modeling will be conducted to determine the cost benefit of an integrated membrane reactor that results from fewer pressure vessels and reduced catalyst volumes.

Results

Key milestones were achieved by focusing on the following activities:

1. **Diffusion Barrier (DB) Development -**
Optimization of the DB layer enables thinner Pd membrane formation, lower material cost per unit area of membrane and reduces the membrane area needed. Process improvements included low profile weld techniques and controlled surface finish of the ZrO₂ with a narrow pore size range. The DB process was scaled up to 12" long tubes and a manufacturing facility is being set up capable of producing DB coated tubes up to 1 meter in length. Obvious cost reductions will occur due to amortization of set up labor over larger quantities and more mechanization of the process steps.
2. **Pd-Alloy Membrane Development and Testing**
- Membrane synthesis process improvements included fabrication methods for PdRu and PdRuAu alloy compositions, lowering the temperature of air oxidation step to increase hydrogen flux

and selectivity without increasing leak rate, and development of a leak repair method to increase the selectivity of the membranes without adding significant thickness to the membranes. The membrane synthesis process is reproducible as evidenced by a large number of membrane samples produced with varying alloying gold content in a narrow thickness range (Figure 1). Laboratory-scale membrane testing focused on determining the effect of major components in the synthesis gas, especially steam and CO, as well as trace contaminant such as H_2S . As shown in Figure 2, the steam effect was negligible whereas CO exhibited minor but reversible influence on hydrogen flux reduction at 400°C. Performance of Pd and Pd-Au membranes was evaluated by adding H_2S to a WGS feed mixture at 400 and 450°C. As shown in Figure 3, Pd-Au membrane, even with only 1% Au, was more resistant to 5 ppm H_2S and the poisoning effect was less at the higher temperature of 450°C. At 25 ppm H_2S , although the hydrogen flux for the PdAu membrane decreased by over 50% the reduction was

FIGURE 1. Reproducibility of Membrane Synthesis Process to Produce a Narrow Thickness Range

FIGURE 2. Effect of Steam and Carbon Monoxide on Membrane Hydrogen Flux Rate

FIGURE 3. Effect of H_2S on Pd-Alloy Membranes

found reversible. Pd membranes were also tested for performance stability against thermal cycling over 50 thermal cycles of 50°C to 400°C and were found to retain both high flux and selectivity.

Two larger scale mixed gas test stands were fabricated, installed, and have been started up to perform sensitivity analyses to WGS reaction impurities as well as to conduct long term durability testing, respectively. The long-term durability tests in synthesis gas environment have just begun.

- High-Pressure WGS Mixture Testing** - Two Pd-alloy membranes were tested in a pilot-scale high pressure environment typical of synthesis gas after the WGS reaction. (This testing was conducted at TDA Research facilities.) The data summarized in Table 2 and Figure 4 show that high hydrogen flux was observed for both membranes, up to 245 SCFH/ft². The feed gas contained: 50% H_2 , 1% CO, 30% CO_2 , 19% H_2O at 400°C, with a differential pressure across the membrane of 170 psi. The average hydrogen permeate purity was 99.96% for membrane #199. Difficulties in controlling the feed pressure caused the observed oscillations in the flux and hydrogen purity at the end of this test and limited the test duration to 75 hours.

TABLE 2. Membrane Performance in WGS Conditions

CSM Membrane Sample #	201	199
Performance		
Pure Gas (SCFH/ft ² atm ^{0.6})	303	331
Mixed Gas (SCFH/ft ² atm ^{0.5})	219	149
Flux - Mixed Gas (SCFH/ft ²)	245	216
H_2 Recovery (%)	67	60
Purity (%)	99.5	99.96
Test time (hrs)	120	75

Although these tests indicated hydrogen recoveries of 60 and 67%, modeling indicates that a H_2 recovery of >80% can be achieved in part by optimizing flow rate and increasing the pressure of the feed stream. Maximum achievable hydrogen recovery is dictated by process operating conditions rather than membrane performance characteristics. Controlled laboratory mixed synthesis gas testing demonstrated hydrogen recoveries greater than 80% by appropriate selection of permeate and feed side pressures.

4. **Cost and Economic Analysis** - Techniques for fabricating a multi-tube module were reviewed and preliminary evaluation of module design, fabrication techniques and materials show that less than \$1,000 per ft² of area membrane module cost is achievable in high volume (>1,000 units) production. High temperature Pd-alloy membranes may be integrated in a conventional natural gas steam reforming process or in reforming of BILF fuels such as ethanol. Cost analysis was conducted in collaboration with DTI using their H2A model modified to include a membrane reactor process for ethanol reforming. Membrane reactor costs are determined by the membrane performance (flux rate) as well as operating parameters (hydrogen recovery). The results show that the capital cost of the membrane unit is a small fraction of the capital cost of the reforming system, and therefore has a very minor influence on the cost of hydrogen produced. Hydrogen recovery on the other hand determines the yield of hydrogen per unit amount of feed stock (ethanol) and therefore significantly influences the operating costs of hydrogen production. This analysis indicated that separation

factor rather than the hydrogen flux rate is a stronger determinant of the hydrogen production cost. Slightly thicker membranes with a tradeoff for greater selectivity and durability over membrane flux may thus be preferable. The economic analysis indicated that the membrane-based hydrogen production process can potentially reduce the cost of hydrogen to below \$3/kg meeting DOE's target.

Conclusions

- The DB substrate process is being finalized and a manufacturing facility is being established.
- Improvements were made in membrane synthesis process and membranes were evaluated for their performance in synthesis gas environment in presence of contaminants.
- High hydrogen purity was demonstrated in high pressure WGS environments.
- The membrane cost and economic analysis indicated hydrogen recovery to be more influential than hydrogen flux with a slightly favorable tradeoff for a little thicker membrane. Membrane synthesis process is capable of producing membranes in the appropriate thickness range.
- Estimation of module costs indicated that less than \$1,000 per ft² of module area cost is achievable and the membrane-based hydrogen production process can potentially reduce the cost of hydrogen to below \$3/kg meeting DOE's target.

Future Plans

- Membrane synthesis process will be finalized and scaled up for manufacturability.
- Mixed gas testing of the membranes will be conducted using the two test stands to determine long term membrane performance at various operating conditions of feed pressure, permeate pressure, gas composition, contaminant composition (especially H_2S) and hydrogen recovery. The membrane performance data collected from these tests will be used for system economic and energy modeling analysis.
- The cost of distributed H_2 target will be demonstrated by incorporating the performance data obtained on the membrane in the membrane reactor H2A computer model to calculate the overall cost of this process. Sensitivity analyses will be conducted using this H2A model to optimize the benefit from process integration.

FIGURE 4. Membrane Performance in High Pressure Post-WGS Synthesis Gas Environment

FY 2009 Publications/Presentations

1. Acquaviva, J., “High-Performance, Durable, Palladium Alloy Membrane for Hydrogen Separation and Purification”, Presented at the DOE Annual Merit Review Meeting, May 19, 2009.
2. Singh, R. and Hopkins, S., “Gas Separation Membrane”, Poster Session, AIChE 2008 Annual Meeting, Philadelphia, PA. Nov. 2008.
3. Damle, A.S. and J. Acquaviva, “Steam Methane Reforming in a Membrane Reactor for Hydrogen Production,” Presented at the AIChE Annual Meeting, Philadelphia, PA, November 2008.
4. Way, J.D., “Palladium and Palladium Alloy Membranes for Hydrogen Separation and Production: History, Fabrication Strategies, and Current Performance,” Invited Plenary Lecture, 10th International Conference on Inorganic Membranes (ICIM 10), Tokyo, Japan, August 2008.
5. Gade, S.K., Payzant, E.A., Park, H.J., Thoen, P.M. and J.D. Way, “The effects of fabrication and annealing on the structure and hydrogen permeation of Pd–Au binary alloy membranes,” J. Membrane Science, 340(1-2), 227–233 (2009).

II.C.3 Water-Gas Shift Reaction via a Single Stage Low-Temperature Membrane Reactor

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Contract Number: DE-FG36-05GO15092

Subcontractor:

University of Southern California, Los Angeles, CA

Project Start Date: July 1, 2005

Projected Ended Date: June 30, 2010

Objective

The water-gas shift (WGS) reaction becomes less efficient when the high carbon monoxide (CO) conversion is required, such as for the distributed hydrogen production applications. Our project objective includes:

- Develop a highly efficient and low temperature membrane-based WGS reaction process in a bench scale first, then tested in a pilot-scale and finally demonstrated in a field test unit.
- Screen our existing membranes and then tailor them specifically for the proposed process and reactor.
- Determine hydrogen production cost and define the system integration requirement for commercialization.
- Reduce the capital and operating cost for distributed hydrogen production applications.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

(K) Durability

(N) Hydrogen Selectivity

(O) Operating Temperature

(R) Cost

Technical Targets

Technical targets for microporous membranes are listed below:

- Flux Rate - 100 to 200 scfh/ft² for 10 to 20 bar pressure, respectively.
- Membrane material and all module costs - \$60-80/ft² of membrane.
- Durability - >1,100 hours of testing has been completed.
- Operating capability - 500 psi.
- Hydrogen recovery - 80% (of total gas).
- Hydrogen quality - greater than 95 percent of total dry gas.

Accomplishments

- **Limited Economic Advantages by the Membrane-Based Process.** Our membrane reactor process (HiCON, combining WGS/H₂ separation via carbon molecular sieve [CMS] membranes) delivers minor cost benefit, in comparison with the conventional (WGS + pressure swing adsorber) process according to H2A analysis. Case studies in DOE H2A analysis show similar results. Hydrogen produced at a low pressure is the main cause.
- **Innovative Solution to Deliver H₂ at Higher Pressure.** An innovative process concept to deliver a higher pressure hydrogen product, e.g., 100 psig, from the membrane process has been developed. This innovation reduces the electricity-driven compression requirement and thus the operating cost. Degree of improvement is presented below.
- **Membrane Development/Modifications (2nd Iteration) to Implement Innovation.** Pd thin film supported on our commercial ceramic substrate/module has been developed to implement the above innovation. This Pd membrane is low-cost, steam stable, and able to sustain the high pressure, i.e., ≥300 psig, uniquely qualified for the proposed innovation. Its long term operation stability, e.g., >30 thermal cycles (room temperature to 350°C) and >2 months on-stream (H₂+H₂O), has been demonstrated.
- **Economic Analysis of the Improved Process.** The H2A analysis on the improved process demonstrates

cost savings potential for a typical membrane-based process. Our preliminary, un-optimized analysis (via PRO/II) exhibits ~5% cost reduction by our membrane-based production process. Optimization is presently underway.

- **Pilot-Scale Membrane Bundle/Module Development and Testing.** Pilot-scale membrane bundle/housing has been prepared and tested under multiple thermal/pressure cycles and is ready for field testing. Hydrogen recovery using a pilot-scale module (i.e., 0.1 m², 21 scfh/hr at 50 psig) has been successfully fabricated and its performance is consistent with the results obtained from the single tube bench top unit, e.g., ≥99.5% purity at 93% recovery.
- **Preparation of Hydrogen Separator for Field Testing.** A pilot-scale hydrogen selective membrane/module (150 scfh H₂, 1.5 m²) is currently under preparation, and will be delivered to our end user in June 2009 for field testing using reformat generated from an autothermal reformer (ATR).
- **Applications for Other Reforming Processes with our CMS Membranes.** Our carbon-based hydrogen selective membrane has been upgraded. Its permeate flux is comparable or better than the Pd/Cu foil at the comparable temperature range. Its stability in the presence of contaminants, e.g., H₂S, has been field tested, and is ideally suitable for use with other reformates, where the Pd-based membrane may have a lack of material stability.

Introduction

Membrane separation has been traditionally considered as a simple, low-cost and compact process. Thus, membrane process has been considered under this project as a WGS reactor/separator for enhancing the hydrogen production efficiency for distributed hydrogen production. In this project, we have focused on the development of the technology components required for integrating a membrane reactor process for distributed hydrogen production.

Approach

Our overall technical approach includes three steps as follows:

1. Bench-Scale Verification
 - Evaluate membrane reactor: use existing membrane and catalyst via math simulation.
 - Experimental verification: use upgraded membrane and existing catalyst via bench unit.
 - Validate membrane and membrane reactor performance and economics.

2. Pilot-Scale Testing
 - Prepare membranes, module, and housing for pilot testing.
 - Perform pilot-scale testing.
 - Perform economic analysis and technical evaluation.
 - Prepare field testing.
3. Field Demonstration
 - Fabricate membranes and membrane reactors and prepare catalysts.
 - Prepare site and install reactor.
 - Perform field test.
 - Conduct system integration study.
 - Finalize economic analysis and refine performance simulation.

Results

1. **Evaluation of M&P Hydrogen Selective Pd Membranes:** Our Pd membranes have been comprehensively evaluated under multiple temperature cycles and extended thermal/hydrothermal testing as shown in Figures 1 and 2. The membrane has shown excellent long-term performance stability under thermal cycling between 350 and 25°C and under hydrothermal conditions at 350°C with 25-85% H₂ and steam for the balance. Our cost/performance ratio meets/exceeds the DOE target. More importantly, the membrane is prepared on existing commercial ceramic membrane products; thus the membrane module preparation can be readily developed.
2. **Separation Performance Results of Pd Membranes in Pilot-Scale Modules (0.1 m²):** The H₂ purity and the H₂ recovery ratio obtained from a pilot-scale module meet the specifications required by our end user for fuel processing via ATR and the requirement for distributed hydrogen production via a steam methane reformer (SMR) after post treatment

FIGURE 1. Characterization of M&P hydrogen selective membrane through thermal cycling between 25 and 350°C.

(presented in previous presentations). In addition, the selectivity and permeance obtained from the mixtures above are similar to those obtained from single components, indicating the dilution effect is negligible (Figure 3).

3. **Delivery of High Purity Hydrogen Permeate at Higher Pressure with Minimum/No Parasitic Energy Consumption:** To deliver the hydrogen product at a higher pressure with our proposed process concept, the membrane surface area requirement increases to achieve a similar recovery ratio. Thus a low-cost membrane is a must. Our innovation shows the potential to achieve further cost reductions for the membrane-based process. No optimization has been performed, which will be complete by the end of this project to finalize the ultimate cost savings potential (Table 1).
4. **Field Test Activities in Fiscal Year 2008-2009:** M&P H₂ selective membranes will be field tested for fuel reforming to produce 152 scfh hydrogen for a 5 kWh fuel cell power generation unit.

FIGURE 2. Long-term hydrothermal stability test of our hydrogen selective membrane at 350°C and in the presence of 25-85% H₂ and steam for the balance.

FIGURE 3. Separation performance of M&P hydrogen selective membrane for hydrogen recovery from synthetic reformates generated from ATR and SMR.

TABLE 1. Performance and economic analysis of our hydrogen selective membrane as a WGS membrane reactor with permeate delivered at a high pressure for distributed hydrogen production.

Energy Data	SMR + PSA	Ours
Methane Conversion [%]	82	82
Hydrogen Recovery [%]	75	90
NG Feedstock [NM ³ / kg H ₂]	4.49	4.3
Utilities [kWh/kg/H ₂]	1.11	1.54
Steam Purge Ratio [-]	NA	0.3
Deliver H ₂ Pressure [psig]	300	90
Post Compression [psig]	5,280	5,280

NG - natural gas

NA - not applicable

Specific Item Cost Calculation based upon DOE H2A Studies

Cost Component	Hydrogen Production Cost Contribution (\$/kg), SMR + PSA	Hydrogen Production Cost Contribution (\$/kg), Ultimate MR*	Hydrogen Production Cost Contribution (\$/kg), Ours
Capital Costs	0.45	0.32	0.40
Decommissioning Costs	0.00	0.00	0.00
Fixed O&M	0.16	0.13	0.14
Feedstock Costs	0.91	0.96	0.87
Other Raw Material Costs	0.00	0.00	0.00
Byproduct Credits	0.00	0.00	0.00
Other Variable Costs (including utilities)	0.10	0.19	0.13

O&M - operation and maintenance

Parameters	1 st Stage	2 nd Stage	Cumulative	Single [control]
Feed Pressure [psig]	300	300	300	300
Permeate Pressure [psig]	90	90	90	0
Purge Ratio [% of feed]	18	18	36	0
H ₂ Recovery [%]	74	16	90	90
H ₂ Purity [%]	99.88	99.7	99.849	99.935
Membrane Surface Area [m ²]	1	0.5	1.5	0.63

Conclusions and Future Direction

During this year, we have:

- developed and comprehensively tested low-cost Pd membranes supported on our ceramic substrate,
- demonstrated successfully separation performance of our Pd membrane in pilot-scale units, and
- demonstrated potential to alleviating economic barriers by a membrane-based process with our innovation.

Presently, we are preparing H₂ selective membranes/modules for field testing. For the rest of the project period, we plan to:

- complete the field test for hydrogen separation with our existing end user to demonstrate its commercial viability in the field, and
- select an end-user to complete the field test for the membrane reactor study.

FY 2009 Publications and Presentations

1. Harale, A., Hwang, H., Liu, P.K.T., Sahimi, M., and Tsotsis, T.T., Design Aspects of a Hybrid Adsorbent-Membrane Reactor (HAMR) System for Hydrogen Production,” In Press,, *Chem. Eng. Sci.*.
2. Harale, A., Hwang, H., Liu, P.K.T., Sahimi, M., and Tsotsis, T.T., Experimental Studies of a Hybrid Adsorbent-Membrane.

II.C.4 Novel Low-Temperature Proton Transport Membranes

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Project Start Date: April 2007

Projected End Date: Project continuation and
direction determined annually by DOE

- Long-term stability testing.
- Atomistic computer simulations to identify potential new proton conducting ceramics.

Accomplishments

- Crystal structure and phase identification studies using X-ray and neutron diffraction completed for over 100 samples prepared to date.
- High temperature conductivity measurements in air completed for over 40 samples to date – hydrogen testing is in progress.
- High temperature structure and stability testing by X-ray diffraction completed for several systems in reducing atmospheres.
- Enhanced capabilities for in situ conductivity measurements established with atmosphere control and capability for measuring high conductivity materials.
- Identified new proton-conducting ceramic oxide with strong potential to meet program requirements.

Future Directions

- Expand Analytical Interatomic Potential computer models.
- Refine models of hydrogen transport.
- Determine hydrogen flux as a function of temperature and pressure for candidate compositions.
- Characterize long-term stability of candidate materials under service conditions.
- Develop metal-supported asymmetric membranes using ORNL support tubes.

Objectives

- To develop a novel proton conductor based on $\text{La}_2\text{Mo}_2\text{O}_9$ (LAMOXY) for use as a H_2 separation membrane.
- To explore compositional development, characterization of the electrical properties, chemical stability, hydrogen flux, and thermomechanical properties; neutron analysis of selected materials to better understand the hydrogen transport properties, and evaluation of surface exchange catalysts.
- To synthesize thin asymmetric membranes (<25 microns thick) from candidate materials with and without exchange catalysts for additional flux testing to determine the range of fluxes possible in these materials.

Technical Barriers

This project addresses the following technical barriers from the Production section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) Reformer Capital Costs
- (N) Hydrogen Selectivity

Approach

- Rapid high-purity materials synthesis using a modified combustion synthesis process.
- Structure and properties (particularly hydrogen flux) characterization.

Introduction

Current alkaline earth perovskite high-temperature proton conductors either have low conductivities or are highly susceptible to chemical attack by contaminants such as sulfur (H_2S) and CO_2 . The LAMOXY family of materials is a promising new class of proton conductors with potential as a hydrogen separation membrane.

In Fiscal Year 2004/2005 ORNL demonstrated that LAMOXY, specifically Nb- and W-doped $\text{La}_2\text{Mo}_2\text{O}_9$, are proton conductors at temperatures below 550°C . ***This was a new finding, as no oxide studied to that date had demonstrated significant proton conduction at temperatures less than 500°C .*** Proton conduction in

materials developed by ORNL was confirmed through independent measurements of hydrogen permeation at the New Mexico Institute of Mining and Technology and at the National Energy Technology Laboratory. The low-temperature conductivity was not as high as that of BaCeO_3 ; however, BaCeO_3 is unstable in all CO_2 and H_2S containing environments and as a result has been largely abandoned for membrane applications.

It appears that proton conduction is most pronounced in the alpha-LAMOX phase, a complex polymorph of the fast oxygen-ion conducting cubic beta-LAMOX phase. Additional experiments demonstrated that the low-temperature α -phase of these LAMOX ceramics was much more stable than the high-temperature beta-phase. LAMOX alpha-phase ceramics did not decompose when exposed to reducing environments of N_2 -4% H_2 at $\sim 500^\circ\text{C}$ for over 10 days; in CO_2 at 800°C for over five days; and in humidified N_2 -4% H_2 at 550°C for over 3 days. These limited tests do not prove long-term stability of these materials, but are very encouraging.

Several characteristics of the LAMOX-based proton transport membrane are not well understood. For example, the LAMOX electrolyte must be heated to $\sim 500^\circ\text{C}$ in humidified H_2 before appreciable hydrogen flux can be measured; however, after the electrolyte is 'activated' at 500°C , H_2 conduction persists as the membrane is cooled to temperatures as low as 200°C and possibly even lower. Additionally, after 'activation' the H_2 flux actually increases as the temperature is decreased. The mechanism by which protons migrate through the membrane is not currently understood, nor is the limit of hydrogen uptake. Furthermore, the mechanism of dissociation of the fuel at surface sites is not understood, nor is its impact on the overall flux - surface dissociation is often the rate-limiting step in proton conduction.

Approach

For hydrogen separation applications, hydrogen flux is the single most important performance issue. Present literature suggests that hydrogen flux rates of between 5 and 50 $\text{mL}/\text{min}/\text{cm}^2$ will be required for commercial application of ceramic membranes.

Measurements of electrical conductivity on LAMOX samples revealed a significant increase in conductivity of the low-temperature alpha phase under reducing atmosphere. From these measurements alone the contributions from electrical, oxygen ion, and proton conductivity cannot be distinguished. In FY 2004 preliminary measurements (at New Mexico Tech and the National Energy Technology Laboratory) of hydrogen permeation were made on 3-mm thick samples of W-doped and Nb-doped $\text{La}_2\text{Mo}_2\text{O}_9$. These results were encouraging in that H_2 permeation was confirmed

in both tests, however the magnitude was only about $5 \times 10^{-5} \text{ mL}/\text{min}/\text{cm}^2$.

In order to increase the hydrogen flux, four possible strategies were proposed, and tasks were assigned so that these could be done in parallel to speed development.

- (1) Reduce sample thickness – reduction from mm to μm dimensions will provide a 2-3 order of magnitude increase in flux based on the Nernst equation.
- (2) Increase H_2 pressure differential – initial tests were done at a low Nernst potential: near 1 atm, with dilute H_2 on the source side and inert sweep gas on the other. Such gain is logarithmic, so perhaps only an order of magnitude gain in flux might be realized, and consequently this approach was not pursued as part of the FY 2008 work.
- (3) Increase bulk proton conductivity – modifying the crystal chemistry with substitutional ion dopants could increase the mobility of protons within the structure, and/or alter the ratio of proton to electron conductivity. This approach in other solid oxide fuel cell (SOFC) systems had led to considerable success, but the magnitude of potential improvements are not yet predictable in the LAMOX system.
- (4) Increase H_2 to proton dissociation rate - use of surface catalysts has proven effective in the cerate systems and could provide 1-2 orders of magnitude increase in flux.

Therefore, overall flux gains of 4-5 orders of magnitude appear to be realistically achievable in this system, which would make it comparable to established dense ceramic or cermet membranes, but with improved stability.

Results

To address the primary task of reducing the sample thickness to increase the hydrogen flux, synthesis of thin LAMOX membranes on porous ceramic supports was initiated as thin plates of LAMOX are not mechanically robust. Thermal expansion data collected at ORNL suggested zirconia as a reasonably matched substrate material. Tungsten-doped lanthanum molybdate (W:LAMOX) was screen printed onto porous 8 mol% yttria stabilized zirconia (8YSZ) pellets and sintered. The W:LAMOX material system was selected initially as a baseline for the supported asymmetric membrane task initially due to vast monolithic test data existing on this system. Although full density was not realized initially, thin ($<20 \mu\text{m}$), adherent, and conformal layers were achieved. This success was extended to praseodymium-doped lanthanum molybdate (Pr:LAMOX), which was also successfully screen printed onto porous 8YSZ pellets and sintered (Figure 1). Note the decrease in

FIGURE 1. Scanning electron micrograph of a $\sim 10\ \mu\text{m}$ thick Pr:LAMOX membrane supported on a porous 8 mol% yttria stabilized zirconia substrate.

membrane thickness (to $\sim 10\ \mu\text{m}$) as well as the increase in the density of the Pr:LAMOX layer.

Nb:LAMOX was examined previously, however, concern over its long-term stability and its tendency to form secondary phases resulted in it being dropped as a candidate material. Improved synthesis methods developed during FY 2008 prompted a re-evaluation of this material. It was found that significantly higher sintering temperatures ($>1,250^\circ\text{C}$) were required to achieve greater than 95% theoretical densities in the $\text{La}_2(\text{Mo}_{1.5}\text{Nb}_{0.5})\text{O}_9$ pellets. However, a secondary phase was again found in the Nb-doped samples, even with lower Nb concentrations, so further work on this system was discontinued. In contrast, barium- and dysprosium-doped lanthanum molybdate (Ba:LAMOX, Dy:LAMOX) yielded excellent single-phase material, which allowed study of proton conduction as a function of dopant valence, substitutional site, and concentration.

Ceramic discs of undoped LAMOX, strontium-doped lanthanum molybdate (Sr:LAMOX), Pr:LAMOX and W:LAMOX were prepared, and 4-wire electrical conductivity (consisting of electronic and ionic components) was characterized as a function of temperature in dry and wet air, as well as inert and hydrogen atmospheres. A typical setup is shown in Figure 2, which also shows the reversible effect of reducing atmosphere on the sample appearance. Multiple samples were tested for each composition, with excellent reproducibility.

Pr:LAMOX was examined to determine if the larger ionic radius of Pr compared to La might result in enhanced proton mobility. The electrical conductivity was not significantly different compared to undoped LAMOX, indicating that lanthanum may be readily substituted by other lanthanide elements, but without much change in the conductivity. Tungsten was partially substituted for molybdenum primarily in a successful attempt to improve the sinterability of LAMOX, but these substitutions stabilized the beta-phase to room temperature. Consequently, as confirmed by our conductivity results (Figure 3) hydrogen (i.e., proton) conductivity is a characteristic of the low-temperature α -phase only, and no conductivity increase was observed in the W:LAMOX samples under H_2 .

FIGURE 2. Ceramic disks with electrodes and platinum wires attached in an alumina holder for 4-wire conductivity tests, using the van der Pauw method. Note that undoped LAMOX samples at high temperatures reversibly turn black in hydrogen, and white in air, with no structural or mechanical degradation so long as the maximum temperature is kept below $\sim 550^\circ\text{C}$.

FIGURE 3. Comparison of undoped (LAMOX) and tungsten-doped (W:LAMOX). Note lower conductivity of W:LAMOX, and no change under 4% H_2 , compared with undoped LAMOX.

Flux Measurements: A hydrogen permeation test rig at the University of Cincinnati (UC) was used to make permeation measurements on candidate samples in collaboration with Prof. Junhang Dong. Thick (2-3 mm) ceramic samples were made from the latest materials to conform to the required dimensions of the UC measurement system. The UC tests gave results (Figure 4) comparable to the fluxes measured in 2004 but with improved accuracy.

SOFC Measurements: For hydrogen gas permeation applications, it is important that the electronic conductivity of the electrolyte be high enough to prevent electrons from forming a charge layer at the electrolyte surface that repels diffusion of protons. Conversely, a low electronic conductivity is essential for a fuel cell electrolyte, as the surface electrons generate the voltage across the cell necessary to provide useable power. While our focus is on the separation membrane application, a fuel cell application is still of significant interest to the DOE Hydrogen Program. Though the initial interest in the beta-phase materials was on oxygen-ion transport for fuel cell applications, to our knowledge there are still no published reports showing working fuel cells from this material. Further, the fuel cell characteristics of these materials will provide valuable insight into the relationship between oxygen-ion, hydrogen-ion (proton), and electron conductivity in this system. A single-cell fuel cell test rig was built at ORNL to enable characterization of electrolytes in a cell with air on one side and dilute (4%) hydrogen on the other, at temperatures up to 1,200°C.

Thin ceramic membranes were synthesized by screen printing multiple coatings of LAMOX inks on

FIGURE 4. Test result from UC on single-phase 2-mm thick Pr:LAMOX ceramic.

NiO/8YSZ 30% pore pre-fired disk substrates, followed by firing at 1,050 degrees Celsius. Platinum paste was applied to both sides to attach platinum mesh electrodes, as shown in Figure 5.

The alpha-phase Pr:LAMOX sample cracked, and new tests are in progress. The beta-phase W:LAMOX sample had small cracks in the ceramic seal, compromising the hydrogen seal and leading to a reduced open circuit voltage, but the sample itself remained intact over a week of testing and enabled the first measurements of fuel cell power in the system (Figure 6).

Future Work: The next phase of this study will be to test the hydrogen permeation of the new dense thin (10 μm) supported ceramic membranes to see if the expected gains in permeation are realized. Further fuel cell testing, nuclear magnetic resonance, and permeation testing is in progress.

Review of Progress to Date

- FY 2007: phase-pure bulk made via combustion synthesis.
- FY 2007: thin samples made via tape casting, followed by lamination, pressing and firing.

FIGURE 5. (top) Pr:LAMOX and (bottom) W:LAMOX samples prepared for fuel cell testing with Pt contact and Pt gauze electrodes attached. Disks are ~1 inch diameter.

FIGURE 6. Fuel cell performance of W:LAMOX membrane. The red curve (and right y-axis scale) are Power, and the values range from 0 to 1.4 milliwatt in intervals of 0.2 mW. The blue curve and left y-axis scale is the output voltage as the load is varied.

- FY 2007/2008: inks developed for screen-printing ultra-thin membranes on porous supports.
- FY 2008: successful thin (<20 μm) membranes deposited on YSZ support.
- FY 2007/2008: improvements in ceramic processing have allowed us to synthesize bulk quantities of powders, and establish correct sintering conditions to make dense single-phase membranes.
- FY 2007/2008: W improves sinterability but stabilizes beta-phase; FY 2004 Nb found to generate problematic impurity phases.
- FY 2007: Ba appears good choice to increase oxygen vacancy concentration, but in FY 2008 we find little change in conductivity
- FY 2008: Sr doping found to be similar to Ba. FY 2007/2008 Pr appears good choice with larger lattice parameter and more free volume, but no change in conductivity is observed. Additional work is ongoing.
- FY 2009: Successful thin (<20 μm) membranes deposited on porous Ni/NiO support.
- FY 2009: First successful test results for W-doped (beta-phase) LAMOX in fuel cell application at temperatures between 450 and 900°C.
- FY 2009: Preliminary nuclear magnetic resonance testing is inconclusive.
- FY 2009: First successful test results for W-doped LAMOX in fuel cell application.
- FY 2009: No significant differences observed to date for humidified versus dry 4% H_2 .

Conclusions

A new approach to development of proton-conducting ceramics, combining atomistic modeling and structure-properties characterization was developed at ORNL, through which the LAMOX series of ceramic oxides was identified as a potential proton-conductor. Detailed characterization of these materials has been carried out using X-ray diffraction (phase analysis, crystal structure), in situ high-temperature X-ray diffraction (phase stability), and electrical conductivity in controlled temperature and gas environments. Hydrogen permeation tests were performed at the University of Cincinnati.

Homogeneous powders are now routinely made by combustion synthesis from stock solutions. High quality samples are synthesized by dry pressing of powders, or by tape casting slurries made from these powders, followed by lamination and sintering. Tungsten was initially added to improve sinterability, but improved powder processing methods developed in FY 2008 have enabled undoped samples to be sintered to near theoretical density without tungsten additions. New progress in FY 2009 has enabled thin membranes to be reliably synthesized on porous supports.

New undoped (alpha-phase) samples confirmed previous conductivity results, and new W-doped (beta-phase) material shows no proton conduction (as expected). New Pr-doped (alpha-phase) material shows proton conduction similar to undoped LAMOX. New Ba-doped and Sr-doped (alpha-phase) material show proton conduction similar to undoped LAMOX. Ytria-stabilized zirconia was identified as a suitable material for porous supports, and 10-20 μm thick membranes of LAMOX, Pr:LAMOX, and Sr:LAMOX on porous YSZ have been synthesized.

II.C.5 Ultra-Thin Proton Conduction Membranes for H₂ Stream Purification with Protective Getter Coatings

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Project End Date: September 30, 2009

Objectives

- Increase proton conduction (and therefore hydrogen flux) via synthesis of ultra-thin dense ceramic membranes on microporous supports.
- Incorporate sulfur getter technology into microporous support layer to address impurities in the feedstock.
- Demonstrate the ability of these ultra-thin membranes to separate H₂ at a high flux rate that meets the DOE 2010 target of 250 scfh/ft².

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (K) Durability
- (L) Impurities
- (M) Membrane Defects
- (N) Hydrogen Selectivity
- (O) Operating Temperature
- (P) Flux
- (R) Cost

Technical Targets

This project is studying the efficiency of ultra-thin dense ceramic membranes to separate H₂ at elevated temperatures. Insights gained from these studies will be applied toward the design and synthesis of hydrogen separation modules to meet the following DOE 2010 hydrogen separation targets:

- Flux: 250 scfh/ft²
 - Deposition of an ultra-thin film will enhance the flux rate per square foot by minimizing the time for protons to be conducted through the dense oxide.
- Hydrogen quality: 99.99% of total (dry) gas
 - The conduction mechanism of separation ensures high purity H₂ as only hydrogen is conducted through the gas-impermeable membrane.
- Operating capability: 400 psi
 - The use of a microporous support structure will enhance the ability of the membrane to withstand significant pressure drops.
- Durability: 26,280 hours between membrane replacement
 - Dense ceramics are resistant to steam. The development of a “getter support” on the feed side of the stream addresses other impurities, such as sulfur, and will support a lengthened membrane lifetime.

Accomplishments

- Successfully deposited strontium oxide and titanium oxide separately using atomic layer deposition (ALD); optimization of the alternating deposition conditions of the two materials and subsequent sintering to make a gas tight strontium titanate membrane is underway.
- Successfully narrowed the pores of the support structure using ALD to deposit Al₂O₃ onto the support.
- Confirmed that the entire mass of the 450 Å zinc oxide layer was able to sorb sulfur from H₂S in a gas stream.
- Discovered that the zinc oxide layer was regenerable over many cycles, and due to the tortuosity of the support, no loss of zinc material from the internal surfaces of the support occurred.
- Calculated the sorbent lifetime of the ZnO layer to be 10 hours per square cm of support, or 70 days for a membrane module with 157 cm² of support.

Introduction

Production costs for the high purity H_2 necessary for fuel cells currently are estimated to be \$3.00 to \$5.00/kg – too high to be competitive with current fuels. H_2 separation from the gas mixture that results from reforming of hydrocarbons or gasification is a major cost of production. The current method for large-scale separation proceeds via water-gas shift reactors followed by a pressure swing adsorption unit. Replacing this multi-step process with a membrane module can reduce hydrogen production costs and increase efficiency. This project addresses the separation of high purity H_2 (>99%) from various feed streams using supported ultra-thin membranes of proton-conducting oxides, such as $BaCeO_3$ and $SrTiO_3$. These dense oxide membranes exhibit 100% selectivity, resulting in extremely high purity H_2 . Sulfur impurities that are typical of many feedstocks will be addressed through the deposition of a getter material, such as ZnO , onto the support structure.

We have demonstrated a low-pressure chemical vapor deposition process, ALD, which is capable of conformally coating very high-aspect ratio structures. Efficient vapor transport at low pressure, combined with selective surface chemistry and sequential introduction of reagents, ensures a highly conformal coating and precise thickness control of structures with aspect ratios $>10^3$. Both the getter and the proton conducting materials are deposited in this project using ALD and plasma-assisted ALD methodologies, which are capable of producing layers on the atomic scale in thickness. As thinner membranes generally have higher fluxes, this study is systematically synthesizing and testing membranes over a range of thicknesses. The sulfur getter material, ZnO , will be deposited in a conformal layer on the mesoporous support. This composite design, combining the best characteristics of dense membranes with those of microporous membranes, will exhibit high selectivity owing to gas separation via proton conduction and high flux owing to the thinness of the membrane.

Approach

To reduce the cost of producing high purity hydrogen, we aim to design a multifunctional membrane module – it will both separate pure hydrogen at high flux rate, and eliminate sulfur contaminants. The module consists of a porous support internally coated with a sulfur getter and capped on one side with a thin proton conducting ceramic membrane. We are using a technique called plasma-assisted ALD. While this technique has not been previously used to fabricate membranes, the control of thickness and depth of penetration make it ideal for ultra-thin membrane

creation. The resulting ultra-thin membranes will have improved hydrogen flux over thicker membranes, and allow us to reach the DOE targets. ALD also is used to conformally coat the internal surfaces of the support with ZnO , a known sulfur getter with excellent capacity and reaction rates. By including contamination mitigation in the membrane module, the durability and lifetime of the membrane will be enhanced.

Results

With the carryover funds from Fiscal Year 2008, we determined to focus on the sulfur sorbent portion of the research.

Sulfur Uptake Measurements

Zinc oxide is known to react with H_2S impurities in gas stream to form ZnS . Additionally, ZnO can react in the same manner with other sulfur impurities, such as SO_2 . The capacity, and hence lifetime, of the getter depends on the surface area, thickness, and reactivity of the getter film. Previously, we have demonstrated the ability of the ALD of ZnO reversibly sorb SO_2 and H_2S forming $ZnSO_4$ or ZnS respectively, regenerating ZnO under heating in air. Complete conversion of the ZnO layer was achieved, indicating that the entire mass of the deposited ZnO is available to act as a sulfur getter in this mesoporous structure. The ability to cycle without loss of material was confirmed last year. Seven cycles of sorption and regeneration did not cause decrepitude of the zinc coating; the tendency of this sorption material to agglomerate and then crumble apart appears to be mitigated by the tortuosity of the support.

We have perfected the deposition of ZnO throughout the porous support. The ALD process was modified to be quasi-static, with a 15-second dwell period of the diethyl zinc in the deposition chamber. Completely uniform coating was achieved when the supports were mounted vertically in the chamber (see Figure 1).

To determine the lifetimes of these sorbent materials, we determined the number of moles of ZnO per gram of coated support through thermogravimetric analysis

FIGURE 1. Cross Sections of ZnO -Coated Porous Al_2O_3 Supports (Green indicates presence of Zn .)

(TGA) measurements. In these experiments, a coated support was completely converted to ZnS by flowing in 2% H₂S for 3 hours at 500°C. The complete conversion has been verified using energy dispersive X-ray spectroscopy in past work. The sample was then placed in a TGA and heated under flowing air. The weight loss arising from the oxidation of ZnS to ZnO was recorded. Per square cm of porous support (1 mm thick), there are 1.35×10^{-4} moles of ZnO. In a gas stream with 100 ppm H₂S present, flowing at 3 ml/min, at 700°C, each square cm of coated support would remove the sulfur from the gas stream for more than 10 hours. A tubular membrane and support module system with 2 cm diameter tubes 25 cm in length, or with 157 square cm of coated support would operate for more than 70 days before needing regeneration. A paper containing the results of this work is in progress.

Current work underway aims to confirm these results using breakthrough tests. A ZnO-coated support is sealed into the permeation unit (see Figure 2) using a

FIGURE 2. Permeation Unit 1" (outside diameter, outer tube) and 1/4" (outside diameter, inner tube), Alumina

pyrex O-ring that is melted at 950°C. A gas mixture of 2% H₂S in N₂ flows to a mass flow controller where it can be diluted to 100 ppm H₂S, then continues past the support on the feed side, and a helium sweep gas flows past the support on the permeate side, carrying any cross-over gas to the gas chromatograph for detection. Proper conditions (flow rate and H₂S concentration) that will allow meaningful sulfur breakthrough curves are being investigated.

Conclusions and Future Directions

No additional work is planned owing to lack of funding. Remaining issues that could be investigated include:

- Perfecting the deposition of a gas tight SrTiO₃ membrane with plasma-assisted ALD.
- Investigating the durability of the membrane and support assembly through many heating cycles.

FY 2009 Publications/Presentations

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References

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II.C.6 Membrane Separation—Bulk Amorphous Hydrogen Purification/ Separation Membranes

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Accomplishments

- Evaluated hydrogen flux properties for five commercially available metallic glass materials.
- Evaluated crystallization parameters via calorimetry and X-ray crystallographic phase analysis as a function of temperature and gas environment.
- Kinetic crystallization parameters based on Avrami equation were obtained for the 2826 alloy and compared with literature.
- Baseline permeation properties of the amorphous alloys were characterized by gas phase permeation.
- The impact of crystallization on the permeation was studied in situ by measuring gas phase hydrogen permeation during crystallization.

Objectives

- Demonstrate the feasibility of using metallic glass materials in bulk form for novel advanced hydrogen purification membranes.
- Develop optimized bulk amorphous alloy compositions for hydrogen separation membranes.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) Fuel Processor Capital Cost
- (C) Operation and Maintenance (O&M)
- (F) Control and Safety
- (N) Hydrogen Selectivity

Technical Targets

DOE 2010 Separation Membrane Targets:

- Flux rate: 200 scfh/ft²
- Cost: <\$100/ft²
- Durability: 100,000 hours
- Operating Temperature: 300-600°C
- Parasitic Power: 2.8 kWh/1,000 scfh

Introduction

Separation and purification membranes must have high hydrogen solubility, high diffusivity and catalytic activity on the surface of the membrane. Hydrogen separation as described in this work can be accomplished by the use of bulk amorphous materials (namely, bulk metallic glasses) permeable to hydrogen. The focal point of the SRNL effort will be on the development and optimization of a bulk amorphous material for the dense metallic-based membrane substrate.

The current generation of gas separation membranes is based on palladium/palladium (Pd/Pd) alloys used either independently or in conjunction with porous ceramic supports. Pd/Pd alloys have been known to possess the ability to dissolve considerable amounts of hydrogen and to demonstrate increasing permeability with increasing pressure differential and temperature. However, the major drawbacks to their industrial use are the high cost for Pd, the relatively low flux, and that during cycling above and below a critical temperature an irreversible change takes place in the palladium lattice structure which can result in significant damage to the membrane. SRNL has previously worked with thin section (melt-spun ribbons) of metallic glass materials for membrane applications, however, with the relatively new ability to cast fully amorphous metallic glasses in bulk sections a new opportunity has opened for bulk metallic glasses (BMG) as hydrogen membranes. The ability to readily cast BMG alloys will allow for easier fabrication of membranes – machine thin membranes

from larger BMG casting – and will also ease mass production challenges in comparison to thin section (melt spun) metallic glass ribbons. These BMG alloys have been shown to possess high permeation rates.

Approach

Testing in Fiscal Year 2009 has centered on the determining the crystallization behavior and subsequent impact on hydrogen permeability of commercially available amorphous/metallic glass materials. The permeation of hydrogen through metallic membranes is a multi-function process involving adsorption, dissociation, diffusion, and recombination and desorption. Two of the inherent materials properties that play a critical role in these processes are the solubility and diffusion of hydrogen in the material. Though the long range structure is “disordered” in amorphous materials, the diffusivity has been thought to occur through interstitial mechanisms similar to crystalline materials. The solubility however, should be enhanced in amorphous materials due to the greater density of defects and distribution of sorption sites which can be occupied by hydrogen over a wide range of potential energies. For materials which are partially crystalline one of the critical factors determining the diffusion, solubility and ultimately the permeation properties is the role the secondary crystalline phase play in the composite structure. It has also been shown that the nature of the crystalline phase depends on the gas environment of crystallization or hydrogen content of the material. In order to systematically study the impact of partial crystallization in these materials a variety of compositions were purchased from commercial sources to obtain five Fe, Ni, Co and Zr based metallic glasses. These samples were subjected to differential scanning calorimetry (DSC) as a function of temperature under different gas compositions in order to quantify phase transition temperature and energies. X-ray diffraction (XRD) analysis was also performed as a function of temperature and gas composition. Finally, hydrogen permeation properties were measured in situ where crystallization took place during gas phase hydrogen permeation at elevated temperatures.

Results

Metallic glass samples with a nominal thickness of 25 microns in 2 inch wide ribbons were purchased from commercial sources (MetGlas Inc., Conway, SC) with the compositions given in Table 1. A 651 model TA Instruments DSC was used to evaluate crystallization temperatures at scan rates of 10°C/min from 25°C up to 590°C in 4% hydrogen and 96% argon gas flowing at 30 sccm. The instrument was temperature calibrated using an indium metal standard and the nominal metallic glass sample mass was ~8 mg. Permeation test samples were sealed by crimping between two VCR® fittings with a Ag-plated Cu gasket which were then connected to a standard 2.12” CF flanges and helium leak tested to confirm lower than 1×10^{-7} std cc/second at 1 atmosphere pressure. Measurement of the steady-state permeation flux was conducted under sub-atmospheric pressures (400 to 700 Torr), values typically used at the Savannah River Site for hydrogen isotope purification. The measured permeability was 5.3×10^{-9} mol H_2 $m^{-1} s^{-1} Pa^{-1/2}$ for the 2826 alloy at 400°C and 700 torr pressure differential compared to Pd flux of 2×10^{-8} mol H_2 $m^{-1} s^{-1} Pa^{-1/2}$.

In order to examine issues related to membrane crystallization, calorimetric techniques were used to determine the temperature of crystallization and the energy released of the five commercial available Metglas alloys indicated in Table 1 and Figure 1 using a ramp rate of 10°C/min under a flowing argon atmosphere. The 2826 alloy was chosen for further kinetic studies due to availability of literature data on kinetic crystallization parameters for comparison. Kinetic rate parameters were obtained from DSC experiments and Avrami kinetic expressions were used to compare experimental crystallization kinetics with literature. XRD were collected on a theta-theta PANalytical X'Pert Pro X-ray diffractometer using an Anton Paar HTK 1200 high temperature attachment. A summary of the crystalline phase formation in varying temperatures and gas environments is displayed in Table 2.

TABLE 1. Alloy Composition Investigated, Purchased from Metglas Company Inc. and Howmet Research Corporation [6]

Alloy	T _i cryst °C	Fe	B	Cr	Mo	Co	Ni	Si
2605S3A	521	85-95%	1-5%	1-5%	0%	0%	0%	1-5%
2714A	551	7-13%	1-5%	0%	0%	75-90%	1-5%	7-13%
2826	421	40-50	1-5%	0%	5-10%	0.3%	40-50%	0%
2605SA1	504	85-95%	1-5%	0%	0%	0.2%	0.2%	5-10%
Zr Alloy	471	Proprietary

FIGURE 1. DSC performed on metglass alloys at 10°C/min under flowing Argon atmosphere 30 sccm from 25°C to 590°C.

TABLE 2. Summary of Identified Phases in 2826 Alloy

Compound	Formula	5°/min in He (°C)	5°/min in 4% H ₂ in He (°C)	5°/min in Air (°C)
Tetrataenite	FeNi	400-710	350-710	350-650
Boron Iron Nickel	Fe _{11.5} Ni _{11.5} B ₆	500-710	500-710	450-550
Boron Iron Molybdenum	Mo ₂ FeB ₂	?-710	?-710	
Iron Oxide Borate	Fe ₂ O(BO ₃)			450-710
Iron Borate	Fe(BO ₃)			500-710? ^a
Molybdenum Iron Oxide	Mo ₃ Fe ₃ O			500-710
Hematite	Fe ₂ O ₃			650-710
Nickel	Ni			?-710
Kamiokitei	Fe ₂ Mo ₃ O ₈			?-710 ^b
Sassolite ^c	B(OH) ₃	Residue only	Residue only	
Isostructural variation of Pinakioite ^c	(Mg,Mn) ₂ Mn(BO ₃) ₂	Residue only		

a) FeBO₃ could be present at 710°C in air. Its presence would be masked by the large hematite peaks.

b) Fe₂Mo₃O₈ was found only in the high temperature XRD residues at concentrations, which are too low to detect on the high temperature stage. It is assumed that it develops above 500°C.

c) Formed during the cool down cycle as air infiltrated the camera. The gas cylinders had been valved off to conserve gas.

For the 2826 alloy, DSC indicates a crystallization temperature of ~420°C which is identified by XRD as a FeNi face centered cubic phase. Kinetic estimates of crystallization suggested that at 400°C the 2826 alloy would completely crystallize in less than 1 hour at temperature limiting the operating window of this

material in gas separation applications. However, the energy release determined by DSC for the crystallization event at 420°C is significantly less than other alloys and XRD of the material near 400°C after 1 hour showed evidence of a large fraction of remaining amorphous phase. Isothermal XRD measurements presented in Figure 2 were carried out at 400°C over a 3-hour duration demonstrated that limited crystallization (30% volume crystalline phase fraction) occurs over this extended period. These crystallization studies were compared with dynamic permeation measurements. In the dynamic measurement displayed in Figure 3, the permeation flux is directly proportional to the measured hydrogen partial pressure. Changes in the slope of this curve, dP/dt indicates apparent changes in the hydrogen flux. The hydrogen permeation at 400°C is seen to decrease slightly over the first hour, and then reaches steady-state values over the following 2 hours concurrent with crystallization measurements.

FIGURE 2. Isothermal XRD measurements for 2826 alloy at 400°C over 3 hours indicating 30% volume fraction crystallinity and remaining amorphous structure.

FIGURE 3. Dynamic permeation measurement, pressure versus time for 2826 alloy at 400°C.

Conclusions and Future Directions

Conclusions

- Commercially available metallic glass membrane materials have been demonstrated to possess permabilities/fluxes on par with Pd-based membrane materials.
- Metallic glass membranes have been demonstrated to provide efficient and effective separation of hydrogen from a mixed gas feed stream.
- DSC and XRD at elevated temperatures show a partial transformation of 2826 amorphous alloy to cubic FeNi crystalline phase (30% by volume) at temperatures near 400°C.
- Dynamic permeation measurements showed this crystallization behavior reduces the flux during the first hour when crystallization occurs and then stabilizes (due to stable amorphous/crystalline phase fraction co-existing) over longer time periods up to 3 hours.

Future Work

- Thin film metallic glass membrane fabrication on porous substrates by sputter deposition.
- First principles modeling in order to investigate compositional effects in metallic glass systems.
- Contaminant effects on hydrogen separation (CO, H₂S etc.).

FY 2009 Publications/Presentations

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4. P. Korinko, K.S. Brinkman, T.M. Adams, G.B. Rawls, *Development of a Non-Noble Metal Hydrogen Purification System* TMS Annual Meeting conference proceedings, symposium Materials in Clean Power Systems IV: Clean Coal-, Hydrogen Based-Technologies, TMS Annual Meeting, San Francisco, CA Feb 15-19 2009.
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6. K. Brinkman, E. Fox, P. Korinko, T. Adams, *Hydrogen Permeation Properties of Metallic Glass Materials*, National Hydrogen Association (NHA) Annual Meeting, Columbia, SC March 30th-April 2nd, 2009.
7. Stephen L. Garrison, Kyle S. Brinkman, Paul S. Korinko, and Thad M. Adams, *Molecular Modeling of Bulk Metallic Glass Membranes for H₂ Separation/Purification*, at North American Membrane Society (NAMS), Charleston, SC June 2009.

II.C.7 Integrated Hydrogen Production, Purification and Compression System

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Contract Number: DE-FG36-05GO15017

Subcontractors:

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- Ergenics Corporation, Ringwood, NJ
(previously HERA USA)

Start Date: April 1, 2005
Projected End Date: September 30, 2010

Distributed Hydrogen Production from Natural Gas or
Renewable Liquid Feedstocks

- (A) Reformer Capital Costs
- (C) Operation and Maintenance (O&M)

Hydrogen Separations

- (K) Durability
- (L) Impurities
- (M) Membrane Defects
- (N) Hydrogen Selectivity
- (O) Operating Temperature
- (P) Flux
- (R) Cost

In addition, the project addresses the following technical
barrier from Section 3.2.4 related to hydrogen delivery:

- (B) Reliability and Cost of Hydrogen Compression

Technical Targets

Technical Targets and the current progress made
towards achieving the 2010 milestones are presented
Table 1.

TABLE 1. Technical Targets: Distributed Production of Hydrogen from
Natural Gas¹

Characteristics	Units	2010 Target	Current FBMR-MHC Projection
Production Unit Energy Efficiency	%(LHV)	72.0	73.3
Production Unit Capital Cost (Uninstalled)	\$US	900K	1,029K
Forecourt Compressor Energy Efficiency	%	94 (CR = 19.8)	72 (CR = 895)
Compressor Installed Capital Cost (Basis: 1,500 kg/day @ 6,250 psi)	\$/kg/hr	4.0	4.43
Total Hydrogen Cost	\$/gge H ₂	2.50	2.81

¹ The H2A Production tool (http://www.hydrogen.energy.gov/systems_analysis.html) was used for the cost modeling. Economic parameters used were for a production design capacity of 1,500 kg/day of hydrogen: 20 yr. analysis period, 10% internal rate of return after taxes, 100% equity financing, 1.9% inflation, 38.9% total tax rate, and Modified Accelerated Cost Recovery Schedule 7-year depreciation for 2005, 2010, and 2015. A 70% capacity factor was used for 2005, and 2010. A 75% capacity factor was used for 2015. The results for 2005, 2010, and 2015 are in 2005 dollars.

LHV – lower heating value

CR – compression ratio

gge – gasoline gallon equivalent

Objectives

- To demonstrate a low-cost option for producing fuel cell vehicle (FCV) quality hydrogen to meet DOE cost and efficiency targets for distributed hydrogen production.
- To develop a hydrocarbon fuel processor system that directly produces high-pressure, high-purity hydrogen from a single integrated unit by combining a fluidized bed membrane reactor (FBMR) and a metal hydride-based compressor (MHC).

Technical Barriers

This project addresses the following technical barriers listed in the Production section (3.1.4) of the updated version (April 27, 2007) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development & Demonstration Plan:

Accomplishments

- FBMR
 - Redesigned and fabricated new membrane modules using higher quality membrane foils.
 - Conducted FBMR run in January 2009 to verify integrity of components after severe winter weather.
 - Operated FBMR for more than 400 hours, with one week of unattended operation.
- MHC
 - Completed MHC fabrication and shipped unit to Vancouver, Canada for integrated tests.
 - Installed MHC next to the FBMR and field tested MHC to obtain base line data.
- Ran integrated FBMR-MHC campaign.
- Developed advanced prototype (AP) system flow sheet.
- Updated and revised cost models for 100 kg/day and 1,500 kg/day systems.
- Utilized H2A Production Tool to explore production cost sensitivity to key parameters identified during proof-of-concept operations.

Introduction

The DOE has determined that the delivered cost of hydrogen must be in the \$2 to \$3/gge range for hydrogen to be competitive with gasoline as a fuel for vehicles. For small, on-site hydrogen plants being evaluated for refueling stations (the “forecourt”), capital cost is the main contributor to delivered hydrogen cost. This project is based on achieving the target hydrogen cost by combining unit operations for the entire generation, purification, and compression system. It uses a membrane reformer developed by MRT which has H₂-selective, Pd-alloy membrane modules immersed in the reformer vessel, thereby directly producing high purity hydrogen in a single step. The continuous removal of pure hydrogen from the reformer pushes the equilibrium “forward” thereby maximizing reactor productivity with an associated reduction in the cost of product hydrogen. Additional gains are envisaged by the integration of the novel hydride compressor developed by Ergenics, whereby H₂ is compressed from 0.5 bar (7 psia) to 350 bar or higher in a single unit using thermal energy. Excess energy from the reformer provides over 25% of the power used for driving the hydride compressor so that system integration can improve efficiency. Hydrogen from the membrane reformer is of very high, FCV quality (purity over 99.99%), eliminating the need for a separate purification

step. The hydride compressor maintains hydrogen purity because it does not have dynamic seals or lubricating oil.

Following the detailed design and assembly of the main reformer skid presented last year, the work this year was focused on commissioning and testing the main reformer skid and completing assembly of the metal hydride compressor skid. These two skids were integrated to form the first proof-of-concept prototype to demonstrate the technology and to verify the assumptions in our analysis. The proof-of-concept unit is designed to produce 1.35 kg/hr high purity, high pressure (100 bar) hydrogen.

Approach

The project team will integrate the membrane reformer developed by MRT and the hydride compression system developed by Ergenics in a single package. This is expected to result in lower cost and higher efficiency compared to conventional hydrogen production technologies, as follows.

Lower cost compared to conventional fuel processors will be realized by:

- Reduced component count and sub-system complexity.
- Tight thermal integration of all reactions/processes in a single package.
- Thermal metal hydride compression without rotating machinery, which should result in high reliability, low maintenance and low electricity usage.

High efficiency will be achieved by:

- Using H₂-selective membranes within the reformer vessel to directly produce high-purity hydrogen, eliminating losses associated with a separate purifier.
- Using a fluidized catalyst bed to improve heat and mass transfer.
- Using the compressor suction to lower the partial pressure of hydrogen in the reaction zone, which shifts equilibrium to enhance hydrogen production.
- Thermally integrating the hydride compressor with the membrane reactor to reduce compression energy consumption.

Results

- FBMR
 - FBMR operated for over 425 hours, including one week of unattended operation.
 - No membrane degradation observed during runtime.

- Production capacity decreased due to partial deactivation of catalyst resulting from sulfur breakthrough in feed.
- MHC
 - Hydride heat exchanger third stage leaks prevented simultaneous demonstration of full flow with full compression ratio.
 - MHC maintained the design 7 psia suction and 1,515 psia discharge pressures at 75% of full flow and delivered full flow with 7 psia suction and 200 psia discharge, using two of the three stages.
- Integrated System Tests
 - The FBMR and MHC were operated together successfully for 8 hours; FBMR performance was stable and the system was not affected by MHC cycling.
 - Integrated operation was intentionally cut short after determining the low production capacity discussed above could not be increased during the run.
- Identified key cost drivers as membrane thickness and longevity, and MHC efficiency.
- AP Conceptual Design Completed
 - Revised cost model shows that H₂ can be produced at \$3.30/kg.
 - Quantified sensitivity of key parameters to help focus future work.

Conclusions and Future Directions

- Project team recommends the project be re-directed because the current H₂A cost model shows that the cost of H₂ can be reduced by:
 - Addressing key technical issues from Task 2 on full-scale components in a laboratory environment.
 - Long-term testing to prove operability, viability and longevity of key FBMR components.
 - Resolving MHC heat exchanger leakage problem.
 - Proving AP design concepts and cost assumptions through accelerated component testing.

FY 2009 Publications/Presentations

1. U.S. DOE Annual Review, May 19, 2009.
2. Hydrogen and Fuel Cells Canada Conference, June 1, 2009.

II.D.1 Composite Pd and Pd Alloy Porous Stainless Steel Membranes for Hydrogen Production and Process Intensification

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Project Start Date: May 7, 2007

Project End Date: May 6, 2010

cost, fuel cost, etc.), followed by comparative studies against other existing pertinent energy technologies.

Technical Barriers

This project addresses the following technical barriers from the Production section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- Long-term selectivity and flux stability
- H₂ flux targets
- Mixed gas and WGS reaction studies
- Composite membrane reactor (CMR) modeling simulations
- Process intensification
- Adsorbent selection and testing

Technical Targets

A number of composite Pd and Pd/alloy porous Inconel membranes for WGS reactors have been and will be synthesized and their long-term thermal, chemical, and mechanical stability and hydrogen flux and selectivity have been determined. Technical targets and current membranes operational data are listed in Table 1.

Objectives

The primary project objectives are:

- Synthesis of composite palladium (Pd) and Pd/alloy porous Inconel membranes for water-gas shift (WGS) reactors with long-term thermal, chemical, and mechanical durability with special emphasis on the stability of hydrogen flux and selectivity.
- Demonstration of the effectiveness and long-term stability of the WGS membrane shift reactor for the production of fuel cell quality hydrogen.
- Research and development of advanced gas cleanup technologies for sulfur removal to reduce the sulfur compounds to <2 ppm.
- Development of a systematic framework towards process intensification to achieve higher efficiencies and enhanced performance at a lower cost.
- Rigorous analysis and characterization of the behavior of the resulting overall process system, as well as the design of reliable control and supervision/monitoring systems.
- Assessment of the economic viability of the proposed intensification strategy through a comprehensive calculation of the cost of energy output and its determinants (capital cost, operation

Accomplishments

- Successfully synthesized a 4.2- μ m thick, Pd/Inconel membrane and a 7.6- μ m thick, Pd/Inconel membrane.
- Completed long-term hydrogen permeation and the selectivity stability testing of membranes (greater than 175 days or ~4,270 hours). Also completed extended tests of 3,550 hours over the temperature range of 400°C to 450°C. Showed that the helium (He) leak of a 7.6- μ m thick, Pd/Inconel membrane was undetectable, indicating an essentially infinite H₂/He selectivity that remains stable.
- Demonstrated a hydrogen flux of ~166 standard cubic feet per hour (scfh)/ft², which is in close proximity to the U.S. Department of Energy's (DOE) 2010 target, based on a high-pressure (P_{high} =118 pounds per square inch absolute [psia], P_{low} =15 psia, ΔP =103 psia) hydrogen flux measurement at 450°C at the end of 3,550 hours. A small helium leak was detected after 3,550 hours that amounted to 0.016 scfh/ft², corresponding to an H₂/He selectivity

TABLE 1. Projected Technical Targets* and Test Data for a Number of Composite Pd and Pd Alloy Porous

	DOE Targets§		Current WPI Membranes				
	2010	2015	#025R	#027	#029	#031	#032
Flux [scfh/ft ²]	200	300	65.9	36.1	166	26.6	359
ΔP (psi) H ₂ partial pressure (P _{Low} =15 psia)	100*	100*	15	15	100	15	100
Temperature [°C]	300-600	250-500	400	400	450	450	442
H ₂ /He Selectivity	n/a	n/a	~220	~120	∞	~4500	~450
Total Test Duration [hours]	n/a	n/a	1015	~1250	~4500	~2200	~523
Thickness [μ m]	n/a	n/a	4.2 Pd	6.2 Pd/Au ₅ wt%	7.6 Pd	7.0 Pd	3-5 Pd
WGS Activity	Yes	Yes	Not tested	Not tested	Not tested	Not tested	Not tested
CO Tolerance	Yes	Yes	Not tested	Not tested	Yes	Not tested	Not tested
S Tolerance [ppm]	20	>100	Not tested	Not tested	Not tested	Not tested	Not tested
H ₂ Purity	99.5%	99.99%	99.0%	99.5%	$\geq 99.999\%$	99.98%	99.8%
ΔP Operating Capability (Max. System Pressure, psi)	400	800-1000	15**	15**	225**	15**	100**

Membranes for Hydrogen Production

§ DOE-National Energy Technology Laboratory Test Protocol v7 – 05/10/2008.

*Standard conditions are 150 psia hydrogen feed pressure and 50 psia hydrogen sweep pressure.

** Maximum pressure tested; however, the ΔP can be higher since previous WPI membranes were tested up to 600 psi under metal-steam reforming reaction conditions.

of ~6,000 after 4,200 hours of testing. The leak is possibly due to hydrogen embrittlement, caused by the large flow rates of hydrogen at elevated pressures resulting in the temperature of the permeating hydrogen stream to drop below 300°C due to the convective cooling effects.

- Prepared a 7.0- μ m thick, pure-Pd/Inconel membrane via an identical synthesis procedure to validate the re-reproducibility of the long-term selectivity stability (~4,270 hours) results achieved with the 7.6- μ m thick pure, Pd/Inconel membrane.
- Achieved 99% total carbon monoxide (CO) conversion and 89.9% H₂ recovery in a 12.5 μ m thick, Pd-based CMR operated at ~350°C, $\Delta P=200$ psi (P_{Low}=15 psia) H₂O/CO=1.44 and gas hourly space velocity (GHSV_{stp})=150 h⁻¹. Under similar conditions, X_{CO,PBR} and X_{CO,Eqm} were 92.7% and 93.4%, respectively.

Introduction

Hydrogen is viewed as the fuel source for the 21st century. Coal may be converted into hydrogen using gasification technology. Given the abundance, availability, and cost-competitiveness of coal in the

United States, coal will likely play a major role in hydrogen production for the 21st century. The WGS reaction is typically used to increase hydrogen yield from coal gasification. The products from the WGS reaction (carbon dioxide [CO₂] and hydrogen) are separated at high (>95 percent) levels of purity using membranes. Combining the WGS reaction and hydrogen separation reduces capital costs and improves efficiency.

Since the separation of hydrogen in the WGS reaction requires high fluxes, as well as high separation selectivity and ability to operate at elevated temperatures, dense metal membranes, particularly Pd-based membranes are well suited for this type of applications.

The objective of this project is to reduce the number of unit operations required for hydrogen production through process intensification. In collaboration with Adsorption Research, Inc., WPI will produce an advanced synthesis gas (syngas) cleanup system and an asymmetric composite Pd-Pd/alloy membrane integrated downstream of the coal gasifier. The high-pressure CO₂ from the membrane shifter would be appropriate for recycling, sequestration, and/or conversion to industrially useful products. Compared with unsupported metal membranes, the development of an asymmetric composite membrane with a porous support and thin Pd or Pd-alloy dense layers would provide both higher trans-membrane flux and lower Pd loading.

Approach

This project will develop an integrated, cost-effective, hydrogen production and separation process using a unique hydrogen separation membrane for WGS reactors under process intensification conditions. A patented (WPI) membrane synthesis process has been used to synthesize thin layer Pd membranes. The process consists of pre-treatment of the porous metal support, in situ formation of an oxide layer to minimize the inter-metallic diffusion for long-term membrane stability, and surface activation and plating of Pd by electroless plating. Specific targets are for production of a Pd layer around 3–5 μm , as well as successful production of Pd/alloy layers of $\sim 2\ \mu\text{m}$ or less.

The synthesized membranes are characterized for their hydrogen permeation characteristics and potential membrane reactor performance. The characterization will include a determination of the hydrogen mass transfer characteristics associated with the membrane configuration and evaluation of the thermal and mechanical stability properties of the membrane through multiple thermal cycling. Characterizations will be conducted on Pd, Pd/gold (Au), and Pd/copper (Cu) membranes. The hydrogen permeation tests will examine effects of Pd alloy compositions and exposure of the membranes to gas mixtures containing sulfur.

Figure 1 shows the test set-up for measurements of membrane properties and permeation rates.

FIGURE 1. Set-Up for Membrane Properties and Permeation Tests

Results

Hydrogen characterization of composite Pd/Inconel membranes was determined under various conditions. Figure 2 displays long-term H_2/He selectivity and flux over a total testing period of $\sim 3,550$ hours (>147 days) at temperatures up to 450°C (membrane #029).

- High pressure flux measurements of the membrane #029 (7.6 μm thick pure-Pd/Inconel) at ~ 400 and 450°C and at a ΔP of ~ 100 psi ($P_{\text{High}}=115$ psia and $P_{\text{Low}}=15$ psia) led to a H_2 flux of ~ 150 and ~ 166 scfh/ft^2 , respectively.
- The excellent H_2/He selectivity stability of membrane #029 over the temperature range of 300 to 450°C , was successfully reproduced with the membrane #031 (7 μm thick pure-Pd/Inconel).
- At $\sim 450^\circ\text{C}$ and at a ΔP of 15 psi ($P_{\text{High}}=30$ psia), the H_2 flux and the final H_2/He selectivity were ~ 26.6 scfh/ft^2 and $\sim 4,500$, respectively, after a total testing period of $\sim 2,200$ hours (>90 days).

FIGURE 2. H_2/He Selectivity and Flux over a Testing Period of $\sim 3,550$ Hours and Under Different Pressure and Temperature Conditions

- At 442°C and at a ΔP of 100 psi ($P_{\text{High}}=115$ psia), the H_2 flux of the 3-5 μm thick Pd/Inconel membrane #032 was as high as ~ 359 scfh/ft² at the end of ~ 285 hours of testing with H_2 /He selectivity of ~ 450 , which exceeded the DOE's 2010 and 2015 H_2 flux targets.

Conclusions and Future Directions

Membranes developed and tested through this project show excellent long-term H_2 /He selectivity and stability over a testing period of about 3,550 hours. A 99% total CO conversion and 89.9% H_2 recovery in a 12.5 μm thick Pd-based CMR operated at 350°C, $\Delta P=200$ psi ($P_{\text{Low}}=15$ psia) have been achieved.

Future work will:

- Continue WGS reaction and mixed gas testing studies.
- Complete 2010 technical target screening and qualification tests.
- Synthesize thin separation layers to achieve higher H_2 flux using support with minimum mass transfer resistance.
- Continue Pd/Au alloying studies to improve H_2 flux.
- Further refine and improve the CMR model (i.e., 2-dimensional non-isothermal finite element modeling via the Comsol Multiphysics).
- Conduct long-term sulfur poisoning and recovery experiments.
- Continue process intensification and performance assessment analyses coupled with process control strategies.
- Complete building and testing of a pressure swing adsorption system.
- Continue synthesis of new Pd and Pd/Au membranes to improve the H_2 flux.
- Test Pd/Au membranes for long-term H_2 /He selectivity stability at 450°C and sulfur tolerance within the temperature range of 300 to 450°C.
- Initiate economical analysis for the proposed process intensification framework.

FY 2009 Publications/Presentations

- Ayturk, M.E., Kazantzis, N.K. and Ma, Y.H., "Modeling and Performance Assessment of Pd- and Pd/Au-based catalytic Membrane Reactors for Hydrogen Production," Energy and environmental Science, 2, 430 – 438 (2009).
- Ayturk, M.E. and Ma, Y.H., "Defect-Free Composite Pd Membranes with High Temperature Long-Term Stability," in preparation.
- Ma, Y.H., Ayturk, M.E., Augustine, A.S., and Kazantzis, N., "Palladium Membrane Reactor for Water Gas Shift Reaction," Submitted to the Catalysis Today.
- Ma, Y.H., Ayturk, M.E., Augustine, A.S., and Kazantzis, N., "Palladium Membrane Reactor for Water Gas Shift Reaction," Presented at the 9th International Conference on catalysis in Membrane Reactors (ICCMR9), June 28 – July 2, 2009, Lyon, France.
- Ma, Y.H., Kazantzis, N., Ayturk, M.E., Pomerantz, N. and Chen, C.-H., "Synthesis and Long-Term Characterization of Sulfur Tolerant Pd/Cu and Pd/Au Alloy Membranes for Hydrogen production via catalytic Membrane Reactor Applications." Proceedings of the 10th Intl. Conf. on Inorganic Membranes (ICM10), Tokyo, Japan, 2008.

II.D.2 Scale-Up of Hydrogen Transport Membranes for IGCC and FutureGen Plants

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Contract Number: DE-FC26-05NT42469

Project Start Date: October 1, 2005

Project End Date: September 30, 2009.

Planned Phase II will continue till 2014.

(N) Hydrogen Selectivity

(P) Flux

(R) Cost

Technical Targets

TABLE 1. Progress Toward Meeting DOE Targets

Performance Criteria	2010 Target	2015 Target	Current Eltron Membrane
Flux, SCFH/ft ²	200	300	450
Operating Temperature (°C)	300-600	250-500	250-440
Sulfur Tolerance (ppmv)	2	20	20 (prelim.)
System Cost (\$/ft ²)	500	<250	<200
ΔP Operating Capability (psi)	400	800-1,000	1,000
Carbon Monoxide Tolerance	Yes	Yes	Yes
Hydrogen Purity (%)	99.5	99.99	>99.99
Stability/Durability (years)	3	>5	0.9
Permeate Pressure (psi)	N/A	N/A	400

N/A - not applicable

Objectives

Develop low-cost hydrogen separation technology which:

- Produces high purity hydrogen from coal-derived synthesis gas (syngas).
- Retains carbon dioxide (CO₂) at coal gasifier pressures.
- Operates near water-gas shift (WGS) conditions.
- Tolerates reasonably achievable levels of coal-derived syngas contaminants.
- Delivers pure H₂ for use in fuel cells, gas turbines, and hydrocarbon processing.
- Meets U.S. Department of Energy (DOE) technical and economic targets in terms of cost-effectiveness compared to alternative technologies for hydrogen separation and carbon capture.

Technical Barriers

This project addresses the following technical barriers from the Production section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

(K) Durability

(L) Impurities

Accomplishments

- Developed a membrane system that meets or exceeds the 2010 DOE targets for hydrogen flux and selectivity at the desired operating temperature and pressure ranges and performs well at expected carbon monoxide (CO) concentrations.
- Developed ceramic-metallic (cermet) blend materials with comparable performance to palladium (Pd) membranes and tested for more than 500 hours without loss in permeability.
- Designed, constructed, and began operations on high-pressure lifetime skids.
- Improved characterization of membranes leading to a better understanding of preparation and performance.
- Developed alloys for membranes and catalysts leading to improved performance and manufacturability.
- Manufactured and tested 10 high flux and low-cost alloys.
- Demonstrated tolerance to 20 ppm hydrogen sulfide (H₂S) at 340°C and ambient pressure.

- Developed modeling tools to characterize and design membranes/systems.
- Improved membrane-based integrated gasification combined cycle (IGCC) flow sheets showing:
 - Carbon capture >95%.
 - Thermal efficiency 32% for cold gas cleaning and 33.6% for warm gas cleaning; ~6% better than conventional technology.
 - Cost of electricity ~10% better than conventional technology.

Introduction

The objective of this multi-year project is to develop and scale up a membrane-based system enabling >95% carbon capture from an IGCC-based power plant, while simultaneously producing essentially pure hydrogen at high flux. The system and hydrogen transport membranes are designed to operate under a variety of conditions and gas compositions, allowing flexible process design and engineering. Additionally, the hydrogen transport membranes can operate at the temperatures and pressures of WGS reactors, which enable effective integration with upstream and downstream process units. Particular focus is intended to address low-cost hydrogen separation that demonstrates improved tolerance to CO and syngas impurities, such as sulfur and mercury, as well as considerations for materials selection and mechanical configuration, which will lead to improved design and overall cost reduction when compared to conventional technologies. Process engineering and economic studies show that improved thermal efficiency and cost of electricity for plants incorporating this technology are likely.

Approach

This project will develop, test, and screen membrane compositions, preparation techniques, and structures (membrane, catalyst, disks, and tubes) in bench- to small pilot-scale units. This work includes evaluating commercially applicable manufacturing techniques for these systems. In addition to performance testing, detailed analytical characterization and evaluation of the mechanical characteristics of the membranes will be completed. Performance screening will be conducted at commercially applicable conditions (up to 1,000 psig and 250°C to 440°C) and feed compositions, including CO, water (H₂O), CO₂, and hydrogen (H₂).

Another major area of interest is the modeling of the process – from surface kinetics to mass transport models, to system performance, to fully integrated IGCC process and economic models. These models are used to

guide the research and development effort and to ensure that the technology being developed is competitive with conventional and other emerging technologies. The engineering is also being done to design the next phase of the project – evaluation of a process development unit that will be tested on “live” coal-derived syngas in an operating facility.

Results

Eltron has tested dozens of catalyst and membrane alloy compositions during the course of the project. Membrane alloy compositions were evaluated for their ability to maintain high flux at improved mechanical strength and enhance resistance to hydrogen embrittlement. Catalyst alloys were assessed for their impact on flux and resistance to impurities. This work allowed down-selecting the catalyst composition to be used for scaling up to the production phase of the project.

In addition to the membrane alloy and catalyst alloy work described above, the impact of asymmetric catalyst thicknesses and catalyst compositions (on the feed and permeate side of the membranes) is also being investigated. Results show that this also has a significant effect on system performance. These tests will continue so that the membrane performance can be optimized.

Another important variable affecting the performance of the membranes is temperature. This affects both flux and membrane stability. A number of experiments evaluating performance in the range of 250°C to 440°C were performed; these experiments showed that a temperature range of about 320°C to 360°C gives an optimum performance trading off flux versus membrane stability.

Significant efforts to improve the chemical and physical characterization of the membrane have also been undertaken, allowing for the optimization of preparation techniques for making the membranes and understanding the differences in performance between membranes. This enables the project team to set quality control standards for the commercial manufacturing of membranes.

Two high-pressure, lifetime testing systems were designed, constructed, and started. Figure 1 shows H₂ fluxes across the selected membrane at T=340°C and ΔP=400 and 600 psi. Figure 2 is a photo of the skid. This skid contains two trains that are capable of operating under conditions expected in a commercial IGCC power plant. The system will operate up to 450°C, 1,000 psig, and use full WGS feed (including the steam). These will mainly be used to run long life tests of thousands of hours in duration to establish that the membranes perform stably over time. This is the last major technical target to be achieved for Eltron’s membrane system.

A mass transport model was developed that examines the contribution of the different mass transfer resistances to hydrogen transport. The model includes resistances from the boundary layer between the catalyst and the bulk gas phase (on feed and permeate), transport through the catalyst layer (feed and permeate), resistance at the buried interface between the catalyst and the membrane (feed and permeate), and transport through the membrane. Detailed experiments are underway allowing the quantitative contributions of each resistance to the overall mass transport of hydrogen through the system.

Process and economic modeling of an IGCC power plant incorporating Eltron's technology has been completed along with similar modeling for comparison to conventional technology. A block flow diagram

FIGURE 1. Membrane Alloy Permeation Data at $T=340^{\circ}\text{C}$ and $\Delta P=400$ and 600 psig

representing one of the myriad of cases examined is shown in Figure 3. For this case, Eltron's membrane technology is paired with warm gas cleaning technology (to remove sulfur and other contaminants from the syngas). The syngas is generated using a high-pressure General Electric gasifier. Comparison of this flow sheet with the one using a Selexol-based syngas cleaning technology shows several significant benefits, which are illustrated in Table 2. This table shows a comparison of three cases: the first column is an IGCC plant with no carbon capture as a reference. The second column is for pre-combustion capture of CO_2 using Selexol. The third column represents the base case shown in Figure 3. As

FIGURE 2. Lifetime High-Pressure System

FIGURE 3. Pre-Combustion CO_2 Capture with Eltron Hydrogen Membrane Technology

can be seen, the thermal efficiency is improved by more than 6% over conventional technology, while cost of electricity is improved by about 8%.

TABLE 2. Technology Comparison

CO ₂ Capture Method	None	Pre-combustion Selexol	Eltron WGPU & Membrane	Δ Selexol vs. Eltron WGPU & Membrane
Coal Feed (tpd)	5,876	3,258	3,526	268
Net Power (MW)	640	239	318	79
HHV Efficiency	38.2%	27.4%	33.6%	6.2%
% CO ₂ Captured	0%	91.3%	95.3%	4.0%
Cost of Electricity (\$/MWh)	78.0	115.5	106	77.32
Plant Cost (\$/kW)	1,813	2,434	2,292	1,863

WGPU - warm gas cleaning unit; HHV - higher heating value

The fourth column in the table is an attempt to evaluate the Eltron technology on an incremental basis versus the Selexol case. This provides a view of the possible improvements since the syngas cleaning and CO₂ capture technologies are only a small part of the capital cost of an IGCC facility, yet capital costs dominate the economics of the plant. Again, it is shown that with over 95% carbon capture, or 5% more than the conventional technology, Eltron's hydrogen membrane is superior from both a capital and a thermal efficiency viewpoint.

Conclusions and Future Directions

Eltron's hydrogen membranes met or exceeded most DOE 2010 targets in bench-scale operations. Process economic evaluations have shown that they provide significant improvements over conventional technologies for capturing CO₂ and providing high purity hydrogen for an IGCC power plant. Future work required to bring these to commercial reality includes:

- Focus near-term on scale-up work with commercial suppliers on the manufacturing of full-size alloy membranes.
- Perform life testing on new materials as required.
- Understand the impacts of contaminants.
- Maintain and improve techno-economic models.
- Design, build, and operate a 220 lb/day process development unit – planned 2010+ goal.

Special Recognitions & Awards/Patents Issued

1. Hydrogen Transport Membranes – Published U.S. Patent Application No. 11/141/250.

2009 Publications/Presentations

1. CO₂ Capture and Hydrogen Production in IGCC Power Plants, Jack, Doug, Gasification Technologies Conference, October 5–8, 2008.
2. Hydrogen Separation Using Dense Composite Membranes, Part 1: Fundamentals. Michael. V. Mundscha, *Inorganic Membranes for Energy and Fuel Applications*; Arun C. Bose, Editor: Springer: New York, 125-154, 2009.
3. Hydrogen Separation Using dense Composite Membranes, Part 2: Process Integration and Scale-up for H₂ Production and CO₂ Sequestration. David H. Anderson, Carl R. Evenson IV; Todd H. Harkins; Douglas S. Jack; Richard Mackay; Michael. V. Mundscha; *Inorganic Membranes for Energy and Fuel Applications*; Arun C. Bose, Editor: Springer: New York; 155-172, 2009.

II.D.3 High Permeability Ternary Palladium Alloy Membranes with Improved Sulfur and Halide Tolerance

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Contract Number: DE-FC26-07NT43056

Subcontractors:

- David Sholl, Georgia Tech, Atlanta, GA
- Bill Pledger, Idatech, Bend, OR
- Gohkan Alptekin, TDA Research, Wheat Ridge, CO
- Doug Way, Colorado School of Mines, Golden, CO

Project Start Date: May 02, 2007

Project End Date: May 01, 2010

Objectives

- Utilize iterative modeling, rapid fabrication, and testing approaches to develop and demonstrate an ultra-thin durable ternary palladium (Pd)-alloy membrane with excellent resistance to sulfur and halogen attack.
- Use density functional theory (DFT) methods to predict hydrogen (H_2) flux through $Pd_{96}M_4$ for M = nickel (Ni), rhodium (Rh), platinum (Pt), niobium (Nb), tantalum (Ta), vanadium (V), magnesium (Mg), and yttrium (Y). Use same methods to predict H_2 flux $Pd_{74}Cu_{22}M_4$ for at least three of the same M .
- Screen initial set ($\leq$ six) of ternary alloys by pure gas (H_2 and nitrogen [N_2]) permeation experiments.
- Fabricate a minimum of 20 membrane specimens with different copper (Cu) concentrations based on Georgia Tech hydrogen transport predictions for the two to three most promising ternary element additions.
- Complete four to five preliminary tests membrane samples at TDA and IdaTech with clean synthesis

gas (syngas) and single impurity additions of hydrogen sulfide (H_2S) and carbonyl sulfide (COS).

- Produce a minimum of 5 ft² of optimized membrane material for use at the Colorado School of Mines (CSM) and TDA and for independent third party evaluation by IdaTech.
- Complete mixture permeation testing with H_2 /carbon monoxide (CO) and H_2 / H_2S binary mixtures with best three samples from the final optimization study.

Technical Barriers

This project addresses the following technical barriers from the Production section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- Hydrogen Embrittlement
- Poisoning of Surfaces
- Impurities in Hydrogen

Technical Targets

Year 1

- Use DFT methods to predict H_2 flux through $Pd_{96}M_4$ for M = Ni, Rh, Pt, Nb, Ta, V, Mg, and Y. Use the same methods to predict H_2 flux $Pd_{74}Cu_{22}M_4$ for at least three of the same M .
- Screen initial set ($\leq$ six) of ternary alloys by pure gas (H_2 and N_2) permeation experiments.

Year 2

- Fabricate a minimum of 20 membrane specimens with different Cu concentrations based on Georgia Tech hydrogen transport predictions for the two to three most promising ternary element additions.
- Complete four to five preliminary tests of membrane samples at TDA and IdaTech with clean syngas and single impurity additions of H_2S and COS.

Year 3

- Produce a minimum of 5 ft² of optimized membrane material for use at CSM and TDA and for independent third-party evaluation by IdaTech.
- Complete mixture permeation testing with H_2 /CO and H_2 / H_2S binary mixtures with best three samples from the final optimization study.

Table 1 lists current test information for a number of membranes and compares it with U.S. Department of Energy (DOE) target values.

TABLE 1. Progress towards Meeting DOE Targets

Performance Criteria	2010 Target	2015 Target	SwRI® Membranes
Flux (scfh/ft ²)	200	300	210
Operating Temperature (°C)	300-600	250-500	200-500
Sulfur Tolerance (ppmv)	2	20	50
System Cost (\$/ft ²)	500	<250	
ΔP Operating Capability (psi)	400	800-1,000	5-150
Carbon Monoxide Tolerance	Yes	Yes	Yes
Hydrogen Purity (%)	99.5	99.99	99.97
Stability/Durability (years)	3	>5	
Permeate Pressure (psi)	N/A	N/A	

N/A - not applicable

Accomplishments

- Efficient and accurate DFT calculation methods were developed to tackle two key challenges:
 - A large number of sites must be sampled with DFT calculations.
 - A statistically valid model that extends DFT data to include all possible sites is needed.
- Tested seven ternary alloys for hydrogen permeation rates under pure gas experiments. Tests were conducted under a range of pressures (five to 150 pounds per square inch gauge [psig]) and temperatures (200°C to 500°C).
- Showed that the addition of four weight percent silver (Ag) to a Pd-Cu alloy membrane improves the permeability by 20 to 25 percent.
- Used computer modeling to predict unique alloy compositions that showed (theoretic) excellent hydrogen solubility and permeability. These compositions were validated through laboratory tests.
- Evaluated promising classes of ternary alloys as membranes under different concentrations of H₂S, hydrogen chloride (HCl), N₂, and other contaminants.
- Successfully tested issues with membrane mechanical strength using the membrane test assembly with 5-um thick foils.

- Achieved 33% higher hydrogen permeability at 400°C than that reported by CSM – due to a suspected difference in membrane conditioning.
- When the membrane assembly cooled and was transferred to the sulfur-poisoned furnace, the membrane failed when it had reached temperature and 100 psig syngas was applied.

Introduction

A critical step in the transition to the hydrogen economy is the separation of hydrogen from coal gasification gases (syngas) or methane (CH₄). This is typically accomplished through membrane separation. Past research has shown that Pd alloys possess great potential as robust and economical membranes. However, the search for the optimal binary or ternary alloys is an involved and costly process due to the infinite number of alloy variations that could be prepared and tested. Recent modeling work at GeorgiaTech using DFT identified several promising ternary alloy compositions with improved hydrogen permeability. These promising ternary alloy compositions, along with various additives at different concentrations, may be tested via DFT calculations and used to guide experimental membrane development efforts.

Self-supporting, dense Pd alloy membranes have exhibited extremely high hydrogen permselectivity and the ability to produce high purity hydrogen feed streams needed for fuel cell applications. The combinations of binary and ternary alloys that can be produced with Pd are theoretically infinite. The use of DFT modeling is an economical and efficient approach to identify promising alloy combinations, which can then be fabricated and evaluated to determine optimum alloy combinations.

Approach

Southwest Research Institute® will lead this membrane advancement effort through the development of materials using advanced physical vapor deposition methods. This includes high power-pulsed magnetron sputtering and plasma-enhanced magnetron sputter deposition to produce thin (<5 micron) Pd alloy membranes. The unique feature of these techniques is the ability to rapidly produce uniform membranes of almost any alloy composition with areas up to 100 in².

CSM will perform initial screening of experimental membranes under controlled atmospheres to confirm that the targeted structures and compositions have been produced. Test results will be used to guide and refine DFT-based modeling and guide the vacuum deposition effort. When one or more promising classes of ternary

alloys have been identified, TDA Research will evaluate these membranes under different concentrations of H_2S , HCl , N_2 , and other contaminants for extended periods up to several hours. Synergistic effects, if any, may also be examined.

Results

DFT-based model predictions are in agreement with literature data for binary alloys indicating:

- Adding Ag or gold (Au) either increases or holds permeability constant relative to Pd.
- Adding Ni or Pt significantly diminishes permeability relative to pure Pd.

Figure 1 displays the DFT-based modeling results for temperature dependence of permeation rates for seven alloys with composition $Pd_{96}M_4$ (at%).

The influence of thickness on the pure hydrogen flux at 400°C and 32 psia hydrogen feed pressure is shown in Figure 2.

The effect of composition and temperature on hydrogen permeability for a number of PdCuAu ternary membranes is displayed in Figure 3.

Results of these studies indicate that:

- All ternary additives strongly enhance permeation relative to $Pd_{70}Cu_{30}$, but all except Ag cause slightly decrease in permeation relative to $Pd_{74}Cu_{26}$.
- More than 37 binary and ternary films have been fabricated with specific compositions to test hydrogen permeability and sulfur tolerance.
- Hydrogen transport appears to be bulk-diffusion limited for all membranes tested at temperatures above 573 K.

FIGURE 1. DFT-Based Modeling Results for Seven Alloys with Composition $Pd_{96}M_4$ (at%)

FIGURE 2. Hydrogen Flux as a Function of Thickness at 400°C, 5 cm $Hg^{0.5}$ Pressure Gradient

FIGURE 3. Hydrogen Permeability for Ternary Alloy Membranes

- PdCuAu has the highest permeability of the ternary alloys tested.
- Binary alloys of Pd with Cu, Ag, Au, and ruthenium (Ru) have comparable permeabilities to literature values.
- In ternary PdCuAu alloys studied, reducing Cu content and raising Au content improves permeability.

Conclusions and Future Directions

So far, more than five membranes have been tested under DOE specified test conditions.

Future work will:

- Produce a minimum of 5 ft² of optimized membrane material for use at CSM and TDA and for independent third party evaluation by IdaTech.

- Complete mixture permeation testing with using DOE specified mixtures with best three samples from the final optimization study.
- Continue model validation with pure hydrogen and test mixtures for ternary PdCuX combinations at different stoichiometry.
- Use the data obtained in Year 1 and Year 2 to optimize membrane form factor (composition, thickness, foot-print, etc.).

II.D.4 Experimental Demonstration of Advanced Palladium Membrane Separators for Central High-Purity Hydrogen Production

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Contract Number: DE-FC26-07NT43055

Subcontractors:

- Power+Energy, Inc. (P+E), Ivyland, PA
- Metal Hydride Technologies, Inc., Burlington, VA

Project Start Date: June 15, 2007

Project End Date: March 31, 2010

- Develop a sulfur-, halide-, and NH_3 -resistant alloy membrane with a projected hydrogen permeance of $25 \text{ m}^3 \text{ m}^{-2} \text{ atm}^{-0.5} \text{ h}^{-1}$ at 400°C and capable of operating at pressures of 12.1 MPa ($\approx 120 \text{ atm}$, 1,750 psia).
- Construct and experimentally validate the performance of 0.1 kg/day H_2 PdCuTM trimetallic alloy membrane separators at feed pressures of 2 MPa (290 psia) in the presence of hydrogen sulfide (H_2S), NH_3 , and hydrogen chloride (HCl).

Technical Barriers

This project addresses the following technical barriers from the Production section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (K) Durability
- (L) Impurities
- (N) Hydrogen Selectivity
- (P) Flux

Technical Targets

This project consists of three parts: atomistic modeling, hydrogen separator fabrication, and membrane separator experimental evaluation. The project has entered the final phase of work where the testing and evaluating of “best of class” hydrogen selective separators will be completed. The progress toward achieving the U.S. Department of Energy’s (DOE) technical targets based on the atomistic modeling predictions and experimental data is shown in Table 1.

Objectives

- Develop and construct hydrogen membrane separators using sulfur-resistant palladium (Pd) alloys and membrane separators using proprietary palladium copper transition metal (PdCuTM) alloys.
- Establish the stability and resistance of proprietary PdCuTM trimetallic alloys to carbon and carbide formation and, in addition, resistance to sulfur, halides, and ammonia (NH_3).

TABLE 1. Progress Toward the Hydrogen Separation Technical Target

Metric	2010 DOE Target	Current Project Status	Notes
Hydrogen Flux	$200 \text{ ft}^3 \text{ ft}^{-2} \text{ h}^{-1}$	$61 \text{ ft}^3 \text{ ft}^{-2} \text{ h}^{-1}$ (P+E alloy) $200 \text{ ft}^3 \text{ ft}^{-2} \text{ h}^{-1}$ (UTRC alloy prediction)	<ul style="list-style-type: none"> • P+E alloy at 600°C; 100 psig H_2 • UTRC alloy predicted to be $200 \text{ ft}^3 \text{ ft}^{-2} \text{ h}^{-1}$ by atomistic modeling at $\approx 475^\circ\text{C}$ with current tube thicknesses
Temperature	$300\text{--}600^\circ\text{C}$	$350\text{--}600^\circ\text{C}$	<ul style="list-style-type: none"> • UTRC ternary alloy limited to 475°C
Sulfur tolerance	20 ppmv	78 ppmv H_2S (P+E alloy) 9 ppmv NH_3 (P+E alloy)	<ul style="list-style-type: none"> • Demonstrated with P+E alloy at 450°C • Demonstrated 487 ± 4 ppmv for 4 hours • Demonstrated 9 ppmv NH_3 for 175 hours
ΔP operating Capability	Up to 400 psi ΔP	280 psig	<ul style="list-style-type: none"> • Facilities and current separator design limited to 20.7 atm (290 psig) testing
CO tolerance	Yes	Yes	<ul style="list-style-type: none"> • Demonstrated up to 13.3% CO at 90 psia total pressure; >9% CO at 304.7 psia
Hydrogen purity	99.5%	99.9999%	<ul style="list-style-type: none"> • P+E manufacturing design and manufacturing ensures no leaks • CO < 1 ppm, S < 15 ppbv desired for fuel cell applications

Accomplishments

- Constructed 10 commercially manufactured hydrogen separators for evaluation.
- Produced five of the separators with the UTRC ternary alloy composition.
- Completed advanced membrane property simulations by atomistic and thermodynamic modeling calculations.
- Performed atomistic modeling calculations to show sulfur and coke resistance of separator alloys.
- Completed experimental hydrogen solubility measurements on alloy tube samples and confirmed atomistic and thermodynamic modeling predictions within a factor of two.
- Evaluated performance of first face-centered-cubic (fcc) PdCu separator.
- Quantified effect of carbon monoxide (CO), carbon dioxide (CO₂), nitrogen (N₂), and water (H₂O) on H₂ permeability. Achieved DOE sulfur targets:
 - 26 scfh/ft² stable flux with 20 ppmv H₂S at 200 psig (100 psig H₂) at 450°C.
 - Operated >100 hours with 33-78 ppmv H₂S with no loss in flux.
- Completed initial technical and economic modeling.

Introduction

This project is focused on increasing the technology readiness level of Pd-based metallic membranes for hydrogen separation from coal-biomass gasifier exhaust or similar hydrogen-containing gas streams. Quantum mechanical atomistic modeling was performed in a previous contract to develop a ternary PdCu alloy for a water-gas shift membrane reactor (WGSMR) in a coal gasifier system. The alloy was based on the concept of making the body-centered-cubic (bcc) phase of a PdCu binary alloy stable at WGSMR temperatures in the presence of high concentrations of poisons such as sulfur. As the bcc phase of PdCu has a much higher hydrogen permeability than the fcc materials, and the fcc materials have been shown to have good sulfur resistance, a stabilized fcc alloy should be able to obtain the high permeability of alloys like Pd-silver (Ag) with the sulfur tolerance of fcc PdCu. Thus, one of the major objectives of this work is to experimentally validate the UTRC PdCu ternary alloy performance. In addition, the best commercially available fcc PdCu alloy from Power+Energy will also be experimentally validated for meeting the DOE technical targets.

Approach

The basic concept for this project is to experimentally validate two different PdCu-based alloys for hydrogen separation. Additional atomistic modeling has been performed to examine performance characteristics, such as resistance to carbon formation. In parallel with the modeling, a new test rig for high pressure separator evaluation has been constructed while separator units of both the Power+Energy and UTRC alloys are manufactured by Power+Energy.

The experimental efforts are divided into two distinct parts: (1) low pressure laboratory screening to quantify basic membrane performance and (2) high pressure testing to quantify durability and poison resistance of the two alloys. The low pressure (<10 atm) laboratory testing objective is to characterize the membrane separator hydrogen permeability as a function of temperature and to quantify the effect of different gas species (CO, CO₂, H₂O, and N₂) on the permeability. The high pressure (>10 atm) testing will involve using an ambient pressure logistic fuel reformer to convert logistic fuel into syngas (hydrogen and CO) which will be compressed and mixed with additional gas containing different concentrations of poisons (H₂S, HCl, and NH₃). The high pressure mixed gas will then be used in 500-hour to 2,000-hour durability tests to quantify the effect of poisons on the hydrogen permeability of both PdCu alloys.

Results

Ten leak-free hydrogen separators were constructed by Power+Energy and delivered to UTRC. Five of these separators contained membrane tubes made with UTRC's ternary bcc PdCuTM alloy composition designed through modeling in a previous DOE contract. The other five separators were made with Power+Energy's best fcc PdCu alloy, which has been demonstrated to be resistant to sulfur concentrations in excess of 100 ppmv. Four separators have been evaluated. Prior to the start of this project, UTRC had already internally evaluated the fcc PdCu alloy and shown it to be resistant to 5 ppmv sulfur and 11 ppmv NH₃. In addition to the 10 separators, Power+Energy also delivered additional membrane alloy tube samples to UTRC for hydrogen solubility testing by Metal Hydride Technologies.

X-ray diffraction analysis was performed on the alloy tube samples to characterize their structures. Figure 1 shows the phase transition diagram and electron backscatter diffraction (EBSD) phase map for binary alloy on surface of ternary alloy. X-ray diffraction confirmed formation of bcc PdCu as predicted. EBSD on an individual tube indicates the presence of a binary Pd alloy covering the surface of membrane. This surface alloy layer was estimated to be 500 Å to 700 Å thick by microprobe analysis. Heat treatments to desegregate/homogenize alloys result in limited improvement.

EBSD phase map

Green = PdG5; Red = PdCu

FIGURE 1. The Phase Transition Diagram and EBSD Phase Map for Binary Alloy on Surface of Ternary Alloy

The UTRC alloy also has a unit cell lattice parameter of approximately 2.99 Å, which is within 2% of the atomistic modeling predictions. Metal Hydride Technologies measured the hydrogen solubility of the tube samples and found the Power+Energy samples to have the solubility expected for that fcc composition. The UTRC alloy samples were found to have a hydrogen solubility of a little more than half that of the thermodynamic and atomistic model predictions. Thus, the bulk composition and structure of the alloy tubes were confirmed to be acceptable.

Figure 2 shows predicted and experimentally derived hydrogen fluxes of the various alloys in this project, as well as the experimentally derived fluxes for a Power+Energy PdAg separator for reference. The lower solid curve represents the experimentally derived flux of the Power+Energy fcc PdCu alloy as a function of temperature. The dotted curve is the original model predicted hydrogen flux for the UTRC ternary alloy which shows that it has the potential to exceed DOE's

FIGURE 2. Predicted and Experimentally Derived Hydrogen Fluxes of the Various Alloys

flux targets above temperatures of approximately 450°C and have a flux performance comparable to PdAg with the sulfur resistance of PdCu at temperatures above 400°C.

PdCu alloy separators were tested for >200 hours with 20 to 90 ppmv H₂S at 410°C to 450°C. Sulfur concentrations at temperatures of 400°C to 500°C have little or no impact on membrane performance. Operation at pressures of 290 psig causes failures in defective membrane tubes. Figure 3 displays hydrogen flux and permeability data for the fcc PdCu alloy.

The best flux of 61 scfh/ft² was measured for pure H₂. Flux for hydrogen gas mixture with >20 ppmv H₂S was identical to sulfur-free flux. Some variations in separator performances were observed. Separator tubes failed at temperatures of 400°C to 770°C and 290 psig pressure. Lowering pressure to <250 psig mitigates the failure.

When the UTRC alloy separators were evaluated to determine their hydrogen permeabilities and fluxes, their performance were found to be lower than that of the Power+Energy alloy. Using a combination of EBSD and microprobe analyses in a scanning electron microscope (SEM), it was determined that most of the surface of the UTRC alloy tubes was covered with a binary alloy of Pd and the ternary stabilizing element. This surface layer was estimated to be approximately 500 Å to 750 Å in depth. Figure 2 shows an EBSD phase map of part of the UTRC alloy sample outer surface. The green areas, which are the majority of the sample, are grains where the binary alloy was identified and the red areas are the <5% of the surface that contains a PdCu phase. Essentially, the binary alloy acts as a diffusion barrier for

FIGURE 3. Hydrogen Fluxes and Permeability of Different Power+Energy PdCu Alloy Separators

hydrogen and reduces the performance of the membranes. Additional SEM/EBSD characterization of the UTRC sample cross section has shown that the ternary alloy identified by X-ray diffraction is present throughout the rest of the sample and the binary phase is not present within the alloy tubes.

Thermal heat treatments in the presence of 6 atm of hydrogen have been unsuccessful in rehomogenizing or desegregating the UTRC alloy separators. The hydrogen flux of those separators continues to be below that of the Power+Energy alloy. As a result, UTRC will be performing experiments to use an appropriate etching solution to remove the surface barrier from the delivered separator units. UTRC and Power+Energy will also look at ways to ensure the binary layer is not present in the final two UTRC alloy separators.

Low pressure laboratory experiments were performed on the Power+Energy alloy. A total of 123 different experimental conditions with different combinations of hydrogen, nitrogen, CO, CO₂, and H₂O were used to evaluate separator performance. The results were quantified in a mathematical permeability model where the effect of each gas was represented by reversible adsorption. The model was tested against an arbitrary gas composition of 66.7% H₂, 7.7% CO, 7.7% CO₂, 7.7% H₂O, and 10.3% N₂, and the model was found to predict the effect of the gas mixture on hydrogen permeability within 5.2% of the experimental results. The effect of H₂S was added to the model based on some of the data shown in Figure 3. The effect of H₂S was found to be orders of magnitude greater than CO which is an order of magnitude stronger adsorber than the other gases.

Conclusions and Future Directions

Ten separators have been successfully constructed with five separators containing the UTRC ternary alloy composition and the other five containing the Power+Energy fcc PdCu alloy. The hydrogen permeability and effect of different gases have been quantified for the Power+Energy alloy. The UTRC alloy

separators have yet to demonstrate the full potential of the ternary composition due to a binary diffusion barrier layer present on the outer surfaces of the alloy tubes.

A new batch of ternary PdCu alloy tubes was produced by Power+Energy with a slightly reduced concentration of the ternary element. The tubes were found to be in the fcc phase as received and showed no trace of a binary phase diffusion barrier on the surface. High temperature X-ray diffraction experiments and a heat treatment at 410°C showed that it is possible to convert these new alloy tubes to the bcc phase, although they may be susceptible to oxidation during high temperature heat treatments. Work is in progress to modify Power+Energy's proprietary heat treatment processing to prevent oxidation by using a hydrogen background gas.

Construction of the high pressure (>10 atm) testing rig using the logistic fuel reformer was completed. More than 300 hours of testing was completed on one

separator with three separators evaluated in the testing rig. The DOE has introduced a new testing protocol for all hydrogen membrane projects. This testing protocol requires somewhat higher pressure testing (particularly for the hydrogen partial pressure) than the UTRC low pressure rig was designed for, as hydrogen and nitrogen are delivered through a house supply system and not via gas bottles. Thus, the low pressure rig was modified to perform DOE's new testing protocol on both types of alloy separators. Once these construction activities are complete, the experimental program will proceed to evaluate the separators' performance as outlined in the Approach section above.

Future work will focus on the fabrication and testing of at least two additional ternary PdCuTM alloy separators. Durability of separators in the presence of H₂S, NH₃, and HCl will be tested and evaluated. Durability for 500 to 2,000 hours will be demonstrated.

II.D.5 The Integration of a Structural Water-Gas Shift Catalyst with a Vanadium Alloy Hydrogen Transport Device

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Contract Number: DE-FC26-05NT42454

Project Start Date: July 1, 2005
Project End Date: June 30, 2009

Objectives

- Develop structural water-gas shift (WGS) catalysts capable of withstanding compressive forces.
- Select vanadium (V)-based alloy hydrogen separation membranes for fabrication of devices by brazing.
- Integrate the WGS catalyst and metallic membranes and testing the integrated device under gasifier conditions.
- Fabricate a modular WGS/membrane integrated device capable of producing 10,000 liters/day of hydrogen from coal-derived synthesis gas (syngas).
- Complete testing of scaled integrated membrane devices based on performance data for testing under coal gasification.
- Develop and test WGS catalyst-membrane modular devices capable of being commercialized.

Technical Barriers

This project addressed the following technical barriers from the Production section of the Hydrogen, Fuel Cells, and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (K) Durability
- (P) Flux
- (Q) Testing and Analysis

Technical Targets

The project contains three separate and important investigations to aid membrane scale-up and integration. Project targets were to meet the DOE goals for hydrogen separation membranes while completing these technical objectives:

- Develop ceramic-based WGS catalysts appropriate for inclusion in pressurized systems undergoing pressure and thermal cycling.
- Develop bonding practices for sealing vanadium alloy membranes to structural alloy components for manufacturability.
- Design integrated systems suitable for scaling to large structures containing monolithic WGS catalysts and metallic vanadium membranes.

TABLE 1. Progress toward Meeting Technical Targets for Hydrogen Separation Membranes

Goal	2010 DOE Target	Project 2009 Estimates
Membrane flux	250 scfh/ft ²	100 scfh/ft ²
Selectivity	99.99	99.999
Pressure	400 psi	400 psi
Recovery	80%	60%
Cost	\$1,000/ft ²	\$600/ft ²

Accomplishments

This project is 95% complete, and the final report is currently being drafted. Two different viable integrated WGS/vanadium membrane device designs were fabricated that should meet scalability issues and performance criteria.

The focus of the chemistry of the WGS catalyst has been on iron (Fe)-aluminum (Al)-chromium (Cr)-copper (Cu)-cerium (Ce)-based systems, including:

- Tested catalysts by impregnation into porous mullite substrates and cordierite monoliths.
- Highest activity and stability have been shown for 75Fe-15Al-8Cr-2Cu.
- Among Fe-Cr-Cu-Ce-oxygen (O) catalysts, those with 4 wt% ceria are the most active and stable for WGS.
- Producing high surface area monoliths of this catalyst series may be problematic due to sintering at higher operational temperatures.
- Obtained and tested multiple vanadium alloys for brazing performance with Cu.
- Developed guidelines based on the brazing tests and analysis of the literature to anticipate the performance of vanadium alloys with respect to hydrogen transport and fabricability based on alloying elements.
- Elements that are potentially positive to both hydrogen transport performance and brazing performance include Ce, Cu, Fe, manganese (Mn), molybdenum (Mo), nickel (Ni), and zinc (Zn).
- Additional alloying elements may be sufficiently advantageous to transport characteristics to overcome their detrimental effect on brazing.
- Brazing results for vanadium and structural alloys, including mild steel, 304 stainless steel, and 9Cr 1Mo steel, were generally excellent.
- Among Fe-Cr-Cu-Ce-O catalysts, those with 4 wt% ceria are the most active and stable for WGS.
- Produced a physical model with three layers of vanadium foil (2.25-inch diameter), and 304 stainless steel, capable of being used as an integrated device (Figure 1).

Introduction

This project responds to a requirement for a system that combines WGS technology with separation technology for coal-derived syngas. The justification of such a system would be improved efficiency and

FIGURE 1. Three-Module Integrated WGS/Membrane Device

lowering cost for hydrogen production. By removing hydrogen from the syngas stream, the WGS equilibrium would force more carbon monoxide (CO) to carbon dioxide (CO₂) and maximize the total hydrogen produced. Additional benefit would derive from the reduction in capital cost of the plant due to the removal of one step in the process by integrating WGS with the membrane separation device.

Approach

The primary goal of this project was to design, fabricate, and test a modular component that integrates the WGS catalyst and the vanadium-based hydrogen selective membrane capable of producing 10,000 liters of hydrogen per day. Modular and integrated WGS/vanadium membrane devices capable of producing hydrogen from coal-derived syngas will be fabricated and tested.

The goal of testing of the scale-up device was to ensure long-term stability of the membrane separation assembly. Short- and long-term performance tests were conducted in the WRI fluidized bed gasifier. This 35 lbs/hr steam/oxygen blown gasifier operates with western coals to produce 175 scfh of hydrogen in a syngas mixture. Additional tests were conducted in a second gasifier producing an alternate range of gas composition and conditions.

Some economic analysis was conducted and data was collected based on predicted cost of manufacturing the scaled membrane unit and the performance data recording hydrogen shift and hydrogen separation. This data is being used to calculate the predicted capital cost of installation and operation of the integrated unit in a commercial facility on a per unit of hydrogen basis.

Results

Significant progress has been made with two different integrated devices. The first device, fabricated with the assistance of Chart Energy and Chemicals, Inc used flat circular membranes of vanadium-palladium alloy supported by porous stainless steel structures (see Figure 1). Each module contained a section of monolithic WGS catalyst and two 4.5-inch diameter membranes. Four modules were required to provide sufficient surface area to supply 10,000 liters/day of hydrogen from a coal gasification source. With the multiple modules, there was some flexibility in the operation of the device to arrange individual pairs of membranes in series or in parallel. Scale-up to larger devices would include both larger diameter membranes and more modules. The largest part of each module was the high-pressure flanges due to the 600-psig application. Permanent fittings would eliminate these flanges and reduce total volume of each module.

The second scale-up unit was based on a “disc and doughnut” design produced by R. Buxbaum of REB Research and Consulting (Figures 2 and 3). In this design, the vanadium alloy membranes were joined in pairs into a structural component capable of withstanding differential pressure. Under a subcontract from WRI, Dr. Buxbaum prepared an integrated, two-membrane unit to contain the monolithic catalyst component. Scale-up of this stackable unit appears straightforward up to a certain number of membranes per module. In this design, all membranes were operated in series. The two-membrane unit were completed and tested in a coal gasifier. Initial pressure tests with helium indicated that the membrane system was leak-free. The first separation tests were conducted in pure hydrogen at 100 psi before moving to the gasifier.

WGS catalyst development was completed with the addition of ceria to the conventional Fe-Cr-Cu oxide catalysts. Since the series of catalysts with small amounts of ceria (2 wt% to 8 wt%) were not as

FIGURE 2. The Scale-Up Unit Based on a “Disc and Doughnut” Design

FIGURE 3. Disc and Doughnut Schematic

effective as the initial ~4 wt% ceria catalyst, apparently due to slight differences in the preparation technique, adjustments were made to the synthesis procedure to attempt to duplicate the original ceria-containing catalyst and to determine if more active and stable catalysts could be produced. WGS catalysts prepared with low levels of ceria was comparable to the improved 15% alumina containing catalysts developed earlier in the project. Ceramic monoliths were developed containing 15% alumina WGS catalyst and incorporation into the two integrated devices described previously. These experiments used a honeycomb mullite structure with multiple coat of the alumina containing WGS catalyst.

Conclusions and Future Directions

- Catalysts have been tested by impregnation into porous mullite substrates.
- Highest WGS activity and stability has been shown for 75Fe-15Al-8Cr-2Cu.
- Small additions of cerium oxide (CeO_2) up to 4% look promising.
- The best catalysts were prepared on mullite monoliths and incorporation into integrated devices.
- Two integrated WGS/membrane devices capable of 10,000 liters/day of hydrogen separation were fabricated and were tested for hydrogen production.
- After preliminary testing under pure hydrogen, both integrated devices were tested on the WRI fluidized bed coal gasifier.

Future work will focus on:

- Commercialization of the WGS catalyst monolith will be pursued with the assistance of a catalyst manufacturer.
- Improvement of vanadium alloy membrane production for large-scale manufacturing.
- Design and fabrication of the 10x assembly based on the economic and performance data for testing under coal gasification conditions.

FY 2009 Publications/Presentations

1. DOE Annual Hydrogen Review Meeting, Washington, D.C., May, 2009; T. Barton.
2. PhD Thesis, Metal Oxide Catalysts for Green Applications, T. Popa, Summer 2009.

II.E.1 Development of Water Splitting Catalysts Using a Novel Molecular Evolution Approach

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Start Date: July 1, 2005

Projected End Date: December 31, 2009

Fuel Cells and Infrastructure Technologies Program
Multi-Year Research, Development and Demonstration
Plan:

- (G) Capital Costs
- (H) System Efficiency

Go/No-Go decision to continue pursuing this approach depends on:

- Ability to measure catalytic signal above noise, and
- Ability to reproducibly synthesize arrays with multiple variable residues.

Technical Targets

Improved Catalytic Performance for Electrolysis:

This project has the goal of generating new, more efficient and more cost-effective catalysts for hydrogen production via electrolysis. Specifically, this work will be applied to reduce the cost of hydrogen to <\$3.00/gge (delivered) at the pump by 2017.

Objectives

Broad Objectives:

- Develop a novel approach to creating molecular metal-binding peptide catalysts for redox reactions based on high throughput synthesis on an array of electrodes.
- Mimick nature's approach to water splitting.
- Reduce the overpotential by 30%.

Specific Objectives (Fiscal Year 2009):

- Optimize high throughput ($>10^4$) peptide synthesis of potential metal-binding peptide catalysts of the water splitting reaction directly on CombiMatrix arrays.
- Optimize the multielectrode measurements of water splitting on the CombiMatrix arrays and quantify the baseline catalysis rate of the system.
- Demonstrate several rounds of optimization for catalytic activity.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Generation By Water Electrolysis section (section 3.1.4.2.2) of the Hydrogen,

Accomplishments for FY 2009

- Multi-step patterned synthesis of peptides in an array.
- Verification of synthesis via direct matrix-assisted laser desorption/ionization (MALDI) spectroscopy on the surface.
- Automation of array synthesis.
- Background current measurements on the arrays.
- Comparing currents from peptides with and without Mn on the arrays.

Introduction

Direct conversion of water to molecular hydrogen and oxygen via electrolysis followed by regeneration of electrical power in a hydrogen fuel cell would be, in principle, an ideal mechanism for the generation and utilization of hydrogen. However, a number of problems still remain to be solved. One of these stems from the fact that the conversion of water to hydrogen via electrolysis using conventional metal electrodes involves a substantial activation energy, necessitating that the reaction be driven by a considerably higher potential than simple thermodynamics would demand. This

overpotential represents a significant energy loss during conversion, impacting the economic practicality of using hydrogen as a fuel in this way.

The biggest part of this overpotential comes from the water splitting reaction at the oxygen evolving electrode (the anode). This is because of the multi-electron nature of the reaction and the high energy, partially-oxidized intermediates that must be formed in order to generate molecular oxygen and protons from water. Fortunately, nature has developed a catalyst, the oxygen evolving complex (OEC) of photosystem II (a complex found in the photosynthetic apparatus of plants), that works with almost no overpotential for this reaction. The OEC contains four manganese atoms that have a structure and chemical environment defined by the surrounding protein. The manganese cluster is directly involved in the redox process and stabilizes the highly reactive intermediates in the oxidation of water. In recent years, a considerable amount has been learned about the characteristics of this complex, including both the redox properties of the manganese atoms at various stages during the four-electron-oxidation of water and the structure of the surrounding protein at moderate resolution.

Approach

Here we propose to use a novel combinatorial biochemical approach to develop manganese binding peptides for modification of the surface of the electrolysis anode used during hydrogen production. The design of these peptides will include features of the OEC and of a model system, developed at ASU, in which bacterial reaction centers lacking the OEC have been modified to bind and oxidize manganese. The approach involves the light-mediated production of large libraries of manganese-binding peptides using a process similar to that employed in the photolithographic generation of deoxyribonucleic acid chips (for example by Affymetrix or CombiMatrix). Each member of the library will be attached to a different microelectrode on a fabricated surface. The current/voltage characteristics of each electrode will be measured in series, looking for the peptide/Mn complexes that result in the lowest overpotential for water splitting. These peptide sequences will then be used as the initial guesses for a subsequent round of molecular evolution, etc. Note that once the peptide-based catalysts are developed in this way, the same types of combinatorial approaches can be used to introduce nonnatural chemical features into the peptides, increasing their resistance to degradation by naturally occurring enzymes and other chemical processes. In principle, similar techniques could also be used to develop catalysts for the hydrogen-evolving cathode (e.g., using hydrogenase as a model) or for the electrodes in hydrogen fuel cells.

Results

Multi-Step Patterned Synthesis of Peptides in an Array

Protection of Terminal Amines – As we seek to synthesize peptides directly on Combimatrix electrode arrays, we have hypothesized that, by protecting α -amines with groups that require milder deprotection conditions (such as dimethoxytrityl and trityl) and protecting side chains with groups that require more stringent removal conditions (like Boc and t-butyl), the side-chain protecting groups will remain stable as we add amino acids to the α -amines during the elongation process. We focused on trityl and dimethoxytrityl protecting groups since they are among the most acid-labile protecting groups available for general organic synthesis. They require approximately 1-3% trifluoromethanesulfonic acid (TFA) for their removal compared to the tert-butoxycarbonyl (Boc) and t-butyl protecting groups, which require 50% and 95% TFA, respectively. We evaluated the stability of trityl and dimethoxytrityl protecting groups in two different electrochemical reagents, 1,2-diphenylhydrazine and hydroquinone. It was found that the trityl groups remained stable in 1,2-diphenylhydrazine solution whereas about 20% were deprotected when exposed to hydroquinone solution. The dimethoxytrityl groups underwent nearly 80% deprotection when exposed to both the 1,2-diphenylhydrazine and hydroquinone solutions without any voltage application.

Based on the stability results of these protecting groups in the two different electrochemical reagents, we decided to move ahead with trityl protection for α -amino groups during manual peptide synthesis and proceeded to deprotect in 1,2-diphenylhydrazine by generation of local acidic conditions due to anodic oxidation. We were able to synthesize peptides involving three electrochemical steps with 40-45% overall yield under these conditions. Four peptides were synthesized in four different regions of a Combimatrix chip. The peptides included control peptides involving no electrochemical steps as well as peptides involving one, two and three electrochemical steps. MALDI spectra showed major peaks corresponding to each of the expected peptides from their respective regions as well as lesser peaks corresponding to peptides synthesized in other regions of the chip (Figure 1). These contaminating peaks may be the result of protons, generated electrochemically from 1,2-diphenylhydrazine, diffusing and deprotecting the trityl groups from amines on silent electrodes. Alternatively, they may be the result of trityl deprotection caused by residual voltage/current in regions where no voltage was applied during each electrochemical step. Even though we obtained unwanted peptides, the ability to synthesize a peptide with three electrochemical steps

FIGURE 1. Region of the chip where a peptide involving three electrochemical deprotection steps was synthesized. Unlabeled peaks represent peptides containing deletions of one amino acid. This experiment does not involve capping after each coupling step; possibly causing some false high yield. The capping step was incorporated after each coupling step in subsequent experiments.

with an approximate overall yield of 41.5% was a major step forward in peptide library synthesis.

The experiment described above proved very difficult to repeat. This led us to move away from manual synthesis and to focus on automating the process in order to create a more reproducible synthesis system. Automation will be described later.

Verification of Synthesis via Direct MALDI Spectroscopy on the Surface

In 2008, we spent considerable effort developing and modifying an approach for performing matrix-assisted laser desorption ionization mass spectroscopy directly from electrode surfaces so that we could determine exactly what peptides had been synthesized or attached to those surfaces. This has been an essential tool in moving forward. Briefly, when we want to perform chemical product analysis on the surface, peptides are coupled or synthesized directly on top of photolabile linkers, previously coupled to the electrodes. After peptides are synthesized or coupled to this surface, the photolabile linkers are cleaved using ultraviolet (UV) light under dry conditions (to avoid diffusion), an appropriate matrix is added to the region of interest and MALDI mass spectroscopy is performed directly from the surface.

Recently, we have tried a different approach, coating a chip containing peptides synthesized on its surface with the α -cyano matrix for MALDI mass spectrometry before exposing it to UV irradiation to cleave the photolabile linker. The concept was that when cleaved, the peptides

should already be co-crystallized with the α -cyano matrix and would be able to be directly analyzed by the MALDI instrument, circumventing the problem of diffusing peptides when matrix is spotted after the UV cleavage of the photolabile linker. Our initial attempts have not resulted in significant desorption of peptide from the surface. We plan to try altering the matrix concentration and composition systematically to see if that will improve the desorption yield.

Automation of Array Synthesis

As mentioned above, there were problems with the reproducibility of manual synthesis. For this reason and for the ability to perform longer syntheses, we automated the hardware/software interface between the Pioneer peptide synthesizer and the Combimatrix Potentiostat electrochemical synthesis chamber. This has allowed us to automate all of the electrochemical steps and eliminate manual initiation of the Echem software to apply the voltages. Once we completed preliminary experiments to confirm the successful integration of the instruments, we attempted to repeat the synthesis involving three electrochemical steps in fully-automated mode. In initial trials, we synthesized a full peptide with three electrochemical steps, though the yield was low at approximately 10% (Table 1). One of the reasons for the low yield of the full peptide was likely the inefficient coupling of the bulky trityl glycine groups used in the synthesis. The MALDI spectra revealed peaks capped with N-acetyl glycine corresponding to each peptide involving electrochemical steps. Experiments to

TABLE 1. Percent yield summary of a region of the chip where a peptide involving three electrochemical deprotection steps was synthesized in automated mode. MALDI not shown but contains unlabeled peaks corresponding to peptides capped with N-acetyl glycine due to inefficient coupling of incoming trityl glycine.

	% Yield
Control Peptide	36.08
Peptide with 1 Echem Step	35.18
Peptide with 2 Echem Steps	19.30
Peptide with 3 Echem Steps	9.40

optimize the overall yield by introducing the trityl group in situ on the α -amines during the synthesis are currently underway.

Comparing Currents from Peptides With and Without Mn on the Arrays

In prior experiments on gold electrodes, we identified peptides from a designed library with catalytic characteristics that we wished to measure on Combimatrix arrays. They included Peptides 2 and 3, Mn-binding test peptides which exhibited increased current values in the presence of Mn ions in solution, and Peptide 4, a non-manganese binding control peptide which showed no increased current values in the presence of Mn ions in solution. We have attempted array-based analyses by synthesizing, in situ, a checkerboard pattern of either Peptide 2 and Peptide 4 on the same Combimatrix slide, or Peptide 3 and Peptide 4 on the same slide, and then performing water electrolysis measurements to examine the influence of the peptides on the electrodes during electrolysis. In general, our MALDI mass spectroscopy results have demonstrated that we achieved a high percent yield of each peptide when we perform synthesis on the CombiMatrix chip, with relatively low ratios of side products in most cases; which gave us confidence to proceed with water electrolysis measurements. Using this approach, we were successful at measuring current as function of voltage for each peptide. Though there was a large, systematic variation in the current as a function of the position of the array element (apparently an artifact of the reading system), the noise at any particular element was relatively small, allowing us to compare in detail the current/voltage curves for each of the peptides. No significant differences were observed between the putative Mn-binding peptides (Peptides 2 and 3) and the control (Peptide 4) (Figure 2).

Background Current Measurements on the Arrays

Since the redox activity of ferrocene is well known, we performed a control by attaching ferrocene to peptides on the array. The idea was to determine

FIGURE 2. A. Selected set of electrodes containing Peptide 2 and Control Peptide 4. B. Plot of current values from all of the electrodes on the chip which contain either Peptide 2 or Control Peptide 4. No significant differences were observed between the putative Mn-binding peptides (Peptides 2 and 3) and the control (Peptide 4). A systematic trend was observed when the curve is blown up, i.e. Figure 3A, is due to the periodic noise from the instrument during measurements.

whether true electrochemical signals associated with the peptides could be distinguished from background. First, to create the ferrocene-containing peptide, ferrocene carboxylic acid was coupled to the alpha amino group of the N-terminus of each peptide by conventional reagents used for amino acid coupling in peptide chemistry. The MALDI spectrometry analysis of the synthesis showed three peaks related to the synthesis, of which one was a full peptide with ferrocene at the N-terminus. Another peak corresponded to the peptide with no ferrocene coupled to it, and the third peak was a peptide containing only one of the cyclopentadienyl rings of the ferrocene coupled at the N-terminus and the rest of the ferrocene molecule getting cleaved under acidic conditions. This synthesis was optimized by increasing the coupling time to increase the intensity of the full peptide with ferrocene.

After optimizing the ferrocene-coupled synthesis to approximately 40% yield as estimated by a MALDI spectrometry analysis (data not shown), we synthesized a range of peptide variants on slides. Some positions on each slide contained ferrocene only. Some contained

peptides that were four amino acids in length with N-terminal ferrocenes, and some contained longer peptides (twelve amino acids) with N-terminal ferrocenes. Some positions on the slide contained neither ferrocene nor peptide. All variants occurred in replicate on regions distributed throughout the slide. We then measured the redox activity on the slides with a voltage sweep. A feature in the oxidative sweep was observed near 0.5 V, somewhat higher than that expected for ferrocene in solution. There was no significant feature in the reductive sweep. The Potensiosense instrument scans the electrodes at fixed voltages and the scan rates are fixed and cannot be altered. Because of this the time between oxidative and reductive sweeps can be lengthy and it is sometimes difficult to obtain reversible oxidation. The oxidative sweep feature only occurred in the ferrocene containing samples and not in the control samples where no ferrocene was coupled (Figure 3). Apparently, the Potensiosense instrument is able to measure

FIGURE 3. A. Region where Ferrocene is directly attached to the surface. B. Control Region with no peptide and Ferrocene. The typical current-voltage curve that we expected to see for ferrocene was not observed. However, a bump in the curve at the right oxidation potential (arrow) for ferrocene was observed, which was lacking in the same region of the control curve where no ferrocene was coupled.

electrochemical signals associated with the peptides if they are large enough. It is likely that for the electrolysis measurements, the platinum is not completely passivated by the combimatrix coating with respect to water oxidation, and at this voltage the background current was too large to detect any small increase due to catalytic activity of the peptide.

Conclusions and Future Directions

During the past year we have:

- Demonstrated multi-step, patterned synthesis of peptides in an array.
- Devised and begun testing an improved method of synthesis verification via direct MALDI spectroscopy on the surface.
- Completed the automation of array synthesis by integrating the fluidics and software our peptide synthesizer with our electrosynthesis instrument.
- Compared currents from peptides, with and without Mn, on Combimatrix arrays.
- Devised and implemented a strategy to evaluate background current measurements on the arrays by incorporating a ferrocene reporter into our syntheses.

Our goals for remainder of the grant period are to:

- Investigate the cause of contaminating peaks on patterned arrays observed during MALDI, possibly resulting from diffusion of protons generated electrochemically from 1,2-diphenylhydrazine that deprotect the trityl groups from amines on silent electrodes, or, trityl deprotection caused by residual voltage/current in regions where no voltage was applied during each electrochemical step.
- Improve the electrochemical deprotection efficiency of trityl protecting groups and enhance the reproducibility of efficient electrochemical deprotection.
- Check the stability of the Boc side-chain-protecting groups during the electrochemical removal of the trityl groups from the α -amino position in order to develop an orthogonal system of protecting groups for peptide synthesis.
- Develop an assay to determine the success of the electrochemical deprotection steps to avoid failure of the synthesis; possibly utilizing fluorescamine for the detection of free amines on the Combimatrix chips during peptide synthesis. Fluorescamine is a dye which possesses a fast amine coupling time (~100 milliseconds) as well as the ability to fluoresce when coupled only to primary or secondary amine functional groups.

- Generate a peptide library using our current capabilities of synthesizing a peptide with two mutant positions.
- Increase the diversity of peptide libraries and measure their catalytic activity.
- Evaluate ability of Potentiostat Instrument to detect catalytic activity as compared to the Cyclic Voltammetry Instrument.

References

1. Fodor, 191 Science 251(4995):767.

II.E.2 High-Capacity, High-Pressure Electrolysis System with Renewable Power Sources

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Contract Number: DE-FG36-05GO15021

Subcontractor:

HyPerComp Engineering, Inc., Brigham City, UT

Start Date: June 1, 2008

Estimated Project End Date: June 1, 2012

Objectives

In this project Avālencc is proposing to develop an enlarged version of our present design that will have 15X the capacity of our single tubular cell. This will be accomplished by first testing a cell at 1,000 psi using conventional pressure containment materials. We will then fabricate and test a single cell at 6,500 psi that uses composite fiber wrapping to achieve the pressure containment. We will then build a sub-scale system containing about 20 cells that will produce about 30 kg/day. After a three-month period testing at the National Renewable Energy Laboratory (NREL), this system will be installed in revenue service in Portland, Maine. These objectives are listed below. The specific technical objectives for the project are listed in Table 1.

Project Objectives

- Achieving at least a 15X increase in the gas production rate of a single high-pressure production cell.
- Demonstrate the high-pressure cell composite wrap which enables significant weight reduction.
- Build and test a 1/10th scale pilot plant.

- Have fabrication ready drawings for full-scale plant (300 kg/day, 750 kW).

Project Technical Objectives

- Determine a manifolding and sealing arrangement for nested cell that satisfies need for H₂ and O₂ gas separation, electrical connection to electrodes, and electrolyte replenishment.
- Determine containment penetration size and design that is compatible with composite wrapped vessel constraints, cell electrode current transfer and flow requirements for gas off-take and electrolyte replenishment.
- Design a functional shape of outer metal jacket for dual purpose:
 - Outer electrode's inner surface.
 - Vessel liner that is the foundation for composite wrap.
- Demonstrate the performance of the nested cell core so that accurate projections of energy use can be integrated into the cost model.
- Demonstrate the ability to implement a composite fiber outer wrap over the nested cell core.
- Produce a pilot plant design for use as a basis for a sound economic analysis of plant fabrication and operating cost.
- Demonstrate the operation and efficiency of the pilot plant:
 - Laboratory testing at Avālencc.
 - Field testing at NREL.
- Have a site ready to accept the completed plant for commercial operation:
 - 100 kW of renewable power in place.
 - Sale or use of the plant products defined.

Technical Barriers

This project addresses the following technical barriers from the Production section (3.1) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (G) Capital Cost
- (H) System Efficiency
- (J) Renewable Electricity Generation Integration (for central)

TABLE 1. Technical Targets and Status

Characteristics	Units	2012/2017 Targets	Aváence Status	Aváence Commercial Projection
Hydrogen Cost	\$/kg H ₂	3.70/<3.00	4.38*	2.84*
Electrolyzer Capital Cost	\$/kg H ₂	0.70/0.30	0.98*	0.33*
	\$/kWe	400/125	2,600*	860*
Electrolyzer Energy Efficiency	% (LHV)	69/74	65*	70*

*Includes capital cost/energy of compression process; LHV – lower heating value

Technical Targets

The goal of this project is to demonstrate the technology and estimate the production, efficiency, and operating cost of a 300 kg/day system. The assumption is that five modules will be used to achieve the 1,500 kg/day level used by DOE in their cost analysis and target cost definitions. The analysis uses a 20 year useful life and annual operating cost estimates of 5% of capital cost. Electricity costs of 3.9 cents/kWhr and an availability of 90% are also used (see Table 1).

Introduction

Aváence has existing technology that is globally unique in its ability to deliver hydrogen directly at storage-ready pressures up to 6,500 psi without a separate compressor. Using an alkaline electrolyte process these Hydrofiller systems integrate the production and compression processes by operating the electrolytic cells at the desired delivery pressure. The systems can interface directly with renewable electricity supplies and have been shown in previous work (DOE Small Business Innovation Research completed in April 2005) that the electrolyzer operates through the full range of voltages output from the connected photovoltaic (PV) array without using any power conditioning equipment. These characteristics result in a renewable hydrogen production and delivery system that is significantly more efficient and reliable, and substantially less expensive than existing commercially available electrolyzer/compressor sets.

These smaller scale Hydrofillers are based on a single cathode/anode tubular cell design with production capability of about 0.1 kg/day. Using the present configuration, this technology is utilized in units (modules) with capacities of up to 10 kg/day by using arrays of individual cells in groups of up to 96. Though effective for small-scale, distributed hydrogen production, 150 modules would be needed to achieve DOE's 1,500 kg/day target for cost comparison. It is unlikely that this ganging of small electrolyzers can meet DOE's cost targets because of the immense

interconnecting tubing requirement, excessive replication of the single cell (15,000), and wasteful repetition of the balance of plant components. A revolutionary design approach to this high-pressure cell core is needed for an order-of-magnitude capacity scale up of the individual electrolyzer modules.

Approach

In this project Aváence is developing an enlarged version of our present design that will have at least 15X the capacity of our present single tubular cell. To achieve this we need to substantially increase the diameter of the individual tubular cell to enable an innovative cell core design – multiple coaxially arranged cylindrical electrodes, nested in a uni-polar configuration – enabling up to 1½ kg/day of production per individual cell. To accomplish this scale-up at 6,500 psi we are partnering with a composite cylinder manufacturer, HyPerComp Engineering Inc. (HEI). They will develop a custom designed containment vessel/cathode using their composite technology expertise that will allow us to effectively increase the diameter of the individual electrolysis cell, enable operation at 6,500 psi, and reduce the cell weight and cost relative to conventional metal containment (similar to what is seen today with composite storage tanks). Ninety-six of these high-capacity cells will now produce a single unit (module) with a production capacity of 150 kg/day.

To complete this development process we are proposing to build a quarter-scale pilot plant of this design composed of 24 cells that will replicate the full plant design and operation, but minimize the cost to DOE for this technology demonstration. The pilot plant will be sent to NREL for verification testing over the last three months of this 30 month project. To effectively utilize the pilot plant at the conclusion of the DOE sponsored portion of this overall program, we are partnering with the Hydrogen Energy Center of Portland, Maine and MaineOxy, an industrial gas supplier, in Auburn, Maine, who are presently teaming in an effort to site the pilot plant in Portland for commercial use, supplying high purity oxygen for industrial sales and hydrogen for use in peak shaving and as transportation fuel. They are presently seeking

State of Maine funding and local investment to install at least 100 kW of renewable power (wind and/or PV) and perform the necessary site preparation for installation and operation. The final result of the project will be a commercially operating 40 kg/day pilot plant integrated with a wind turbine and/or PV Array, and delivering product at 6,500 psi to storage cylinders. Operation of this plant and extensive testing of this and earlier development versions throughout the course of the project will thoroughly document the performance and operation of the technology. This combination of an operating pilot plant and substantial performance and operating data will position this technology for commercialization to a waiting market.

Issues

Work on this project was delayed for approximately eight months while we identify and test a new membrane that can effectively block hydrogen egress into the oxygen byproduct. As an alternative approach we will be testing an approach to recycle the oxygen by-product gas after purification to reduce the hydrogen levels in the oxygen byproduct gas. In addition we are working with electrical isolation hose suppliers to produce a 6,500 psi hose for our system, since the original hose produced for us has shown a gas leakage rate that is unacceptable for efficient operation (though well within the limits of safe environmental operation). As a back up to this we are examining non-flexible electrical isolation arrangements.

Accomplishments

Highlights of the progress are as follows:

- Successfully demonstrated joinery for membrane material.
- The design of the single cell test apparatus was completed.
- The design of the 1,000 psi single cell was completed.
- HEI completed the design of the 6,500 psi containment vessel.
- Fabrication of the test apparatus continued.
- Materials for the 1,000 psi single cell test article were ordered.

We completed our extended testing of the adhesive used to create the seams in the membrane material required to construct the cylindrical membranes for the test apparatus. This testing was performed on our standard configuration membranes in actual electrolyzer operation (28% KOH and 50°C) for over 1,000 hours. Destructive testing revealed that the base material

ripped without the seam failing even after the extended environmental exposure. Figure 1 shows a membrane and the seam (indicated by the black adhesive).

Figure 2 is an example of the detailed design drawings completed so that fabrication of the cell can begin when the ordered materials have arrived. Figure 3 is the designers rendering of the 1,000 psi single cell test article.

We are progressing well on the fabrication of the test apparatus. Figure 4 shows the fabrication of the valve panel for the test apparatus in progress.

Future Work

Over the next year we will complete the fabrication and testing of the 1,000 psi test cell and demonstrate the ability to operate at 6,500 psi. If funding allows we will fabricate and demonstrate the 6,500 psi test cell.

FIGURE 1. Membrane Seam after >1,000 Hours of Testing

FIGURE 2. Typical Cell Design Drawing

FIGURE 3. Rendering of 1,000 psi Single Cell Test Article

FIGURE 4. Valve Control Panel Fabrication in Progress

II.E.3 PEM Electrolyzer Incorporating an Advanced Low-Cost Membrane

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Contract Number: DE-FG36-08GO18065

Subcontractors:

- Virginia Polytechnic Institute and State University, Blacksburg, VA
- Parker Hannifin Ltd domnick hunter Division, Hemel Hempstead, United Kingdom

Project Start Date: May 01, 2008

Project End Date: April 30, 2011

Objectives

Develop and demonstrate advanced low-cost, moderate-pressure proton exchange membrane (PEM)-based water electrolyzer system to meet DOE targets for distributed electrolysis:

- Develop high efficiency, low-cost membrane.
- Develop long-life cell-separator.
- Develop lower-cost prototype electrolyzer stack and system.
- Demonstrate prototype at the National Renewable Energy Laboratory (NREL).

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (G) Cost-Capital Cost
- (H) System Efficiency

Technical targets for this project are shown in Table 1.

TABLE 1. GES Progress toward Meeting DOE Targets for Distributed Electrolysis Hydrogen Production

Characteristics	Units	2012/2017 Targets	GES Status
Hydrogen Cost	\$/kg H ₂	3.70/<3.00	3.97*
Electrolyzer Capital Cost	\$/kg H ₂	0.70/0.30	1.47
	\$/kW _e	400/125	<500
Electrolyzer Energy Efficiency	% (LHV)	69/74	68**

*using H2A model rev 1.0.11; **75% for a single cell
LHV - lower heating value

Accomplishments

- Membrane
 - Demonstrated enhanced dimensionally stable membrane (DSM™) performance. (> Nafion® 1135 membrane).
 - Completed 1,000-hour life-test with DSM™ (@80°C).
 - Projected DSM™ operating lifetime to be approximately 55,000 hours.
- Cell-Separator
 - Demonstrated performance of a low-cost titanium/carbon cell-separator.
 - Confirmed longevity of the carbon/titanium cell-separators.
- Preliminary Electrolyzer System Design Review
 - Completed process and instrumentation diagram (P&ID), process flow diagram (PFD), and system control diagrams.
 - Completed an extensive safety review of electrolyzer system.
 - Completed modeling of electrolyzer capital and operating costs; performed economic analysis using the DOE H2A (rev. 1.0.11) model illustrating cost reductions.

Introduction

The DOE has identified hydrogen production by electrolysis of water at forecourt stations as a critical technology for transition to hydrogen powered vehicles. As hydrogen fuel cell vehicle market penetration increases water electrolysis for hydrogen production at

centralized locations using renewable energy sources will be a part of a hydrogen infrastructure. However, state-of-the-art electrolyzers are not economically competitive for forecourt hydrogen production due to their high capital and operating costs. The cost of hydrogen produced by present commercially-available electrolysis systems is estimated to be \$4.80/kg-H₂, considerably higher than the DOE target of \$3.70/kg-H₂ by 2012 [1]. Analysis of electrolyzer systems performed by GES and others using the DOE H2A model indicate that the major cost elements are the cost of electricity and the high capital costs of electrolyzer stacks and systems.

GES has developed a PEM-based electrolyzer technology that generates hydrogen at moderate to high pressure directly in the electrolyzer stack. The GES technology maintains a high-differential pressure across the PEM, so that oxygen is evolved at near-atmospheric pressure while the hydrogen is produced at elevated pressure.

The goals of the project are to reduce stack and system cost to improve electrolyzer efficiency and to demonstrate electrolyzer operation at moderate pressure.

Approach

To reduce the cost of operating PEM-based electrolyzers, GES is improving electrolyzer stack efficiency through development of an advanced high efficiency, dimensionally stable membrane (DSM™). In addition, an effort has been placed on reducing the cost of the electrolyzer stack via the development of a low-cost, long-life, bipolar stack cell-separator. Further reductions in system capital costs are also obtained by applying commercial production methods to the PEM-based electrolyzer systems. In each of the key development areas, GES and its team members are conducting focused development of advanced components in laboratory-scale hardware, followed by life-testing of the most promising candidate materials. The project will culminate in fabrication and testing of an electrolyzer system for production of 0.5 kg-H₂/hr and validation of the electrolyzer stack and system in testing at NREL.

Successful development of the advanced electrolyzer stack and system will result in a high-efficiency, low-capital-cost electrolyzer that will meet the 2012 DOE cost targets for hydrogen production, assuming high-volume production. This will provide competitively priced hydrogen for delivery at forecourt stations to enable the transition to hydrogen-powered vehicles.

Results

DSM™ Membrane Performance: To improve electrolyzer efficiency, and thereby reduce operating and capital costs, GES is developing an advanced supported

membrane having an ionic resistance comparable to that of a 0.0020- to 0.0035-inch-thick Nafion® membrane, but having significantly improved mechanical properties. This advanced membrane is referred to as a dimensionally stable membrane because the membrane support minimizes changes in membrane dimensions (swelling/contraction) under high-pressure operation and with changes in water content. Performance and durability of the advanced high-efficiency DSM™ was demonstrated in full-size (160-cm² active area) electrolyzer hardware at an elevated temperature of 80°C and differential operating pressure of 300 psid for a period of 1,000 hours, simulating operation in an actual electrolyzer system.

DSM™ performance and durability were assessed by two major characterizations: fluoride release rate (FRR) and polarization performance. Since PFSA ionomer is used as the membrane material and in the binder for the catalyst layer, fluoride loss is a good measurement for PFSA ionomer degradation. An FRR rate of less than 3.0 µg F⁻ ion/hr was measured at the end of the 1,000-hour life test. Less than 10 micrograms F⁻ ion/L (<10 ppb) were found in the cathode side, electro-osmotically transported water. Based on the electrolysis life data and FRR results, the lifetime of the DSM™ is projected to be between 45,000 and 55,000 hours, which exceeds the durability requirements of the electrolyzer system. In addition to its durability, the DSM™ exhibits high cell efficiencies in the range of 75% lower heating value (88.8% higher heating value), operating in the cell voltage range of 1.72 V at a current density of 1,500 mA/cm² (Figure 1).

Polarization scans through a current density range of 3,000 mA/cm² were conducted to evaluate the DSM™ membrane-electrode assembly (MEA) performance under the operating conditions stated above: 80°C, 300 psid. A comparison made between DSM™ and Nafion® 1135 MEAs under similar operating conditions, cathode and anode electrode structures, and in the same

FIGURE 1. 1000-hour Life Testing of DSM™ MEA

160-cm² hardware, show that the DSM™ MEA exhibited lower cell voltages (lower power requirements) and thus higher cell efficiencies (Figure 2).

In addition to the DSM™, a second membrane approach, under development with Virginia Polytechnic Institute, is advanced Bi Phenyl Sulfone hydrocarbon membranes. Initial results obtained at GES have shown that these membranes have high efficiency, high protonic conductivity, excellent mechanical properties and high chemical stability in PEM-based electrolyzers.

Cell-Separator Development: The cell separator is a gas-impermeable conductive sheet that separates the hydrogen and oxygen compartments in the bipolar stack. The separator must be highly conductive, as well as resistant to hydrogen embrittlement and to corrosion in an oxidizing environment. The proven GES high-pressure naval electrolyzer uses a complex multi-layer separator incorporating a conductive compliant member and sheets of niobium and zirconium metal. Zirconium is used due to its high resistance to hydrogen embrittlement. GES has previously evaluated a low-cost, dual-layer titanium cell-separator. Although performance was comparable to that of niobium/zirconium cell-separators, lifetimes were limited to 5,000 hours due to hydrogen embrittlement.

The most promising approach for long-term implementation is coating titanium with a low-cost electrically conductive, embrittlement-resistant carbon coating. The challenge was the development of a pinhole-free, highly adherent coating with the required characteristics. Under the cell-separator development task, GES demonstrated performance (polarization curve) of a low-cost carbon/titanium separator in 160-cm² hardware comparable in performance to a dual-layer titanium separator at 1/40th the cost of niobium-zirconium cell-separators (Figure 3). In addition, life expectancy of the carbon/titanium separator, determined via hydrogen-uptake analysis over a 500-hour period, indicates lifetimes exceeding the 50,000-hour system requirement.

FIGURE 2. Performance and Efficiency of DSM™ vs. Nafion® 1135

Preliminary Electrolyzer Stack and System

Design: The materials and manufacturing methods developed in this project have significantly decreased the electrolyzer stack and system capital cost. As a result of the component and membrane development conducted in this project, the overall projected capital cost of the electrolyzer stack (designed for 330-psig operation) has decreased from greater than \$2,500/kW in 2001 to less than \$500/kW in 2009, with a further projected decrease to <\$400/kW in 2012, assuming successful commercialization of the low-cost manufacturing methods and large-scale production of electrolyzer stacks.

In addition to the overall decrease in parts count per cell and the use of low-cost cell-separators, the preliminary stack design shown in Figure 4 includes two major modifications to the previous hardware; (1) an increase in cell active area from 160 to 290 cm² and (2) the use of a pressurized dome that encloses the electrolyzer stack, which strengthens the stack assembly and provides personnel and equipment protection in the unlikely event of failure. Larger cell active areas reduce the number of cells required to produce a given amount of hydrogen, and thus reduces the stack manufacturing labor and the materials scrap rate. The addition of a *pressurized dome* makes the electrolyzer stack and system a more commercially viable product. Pressure sensors attached to the dome will monitor any decrease/increase in pressure, indicating stack leakage, and the system can then be shut down safely.

GES electrolyzer system designs and Parker Hannifin Ltd. (Parker) hydrogen generator designs have been reviewed and the appropriate aspects of

FIGURE 3. Performance Scans: Carbon/Titanium vs. Dual-Layer/Titanium

FIGURE 4. Preliminary Stack Design

these designs incorporated into the prototype system design with a focus on eliminating and replacing costly components and improving balance-of-plant (BOP) efficiency. Our subcontractor, Parker has completed the PFD and P&ID, as well as the control logic diagrams. As part of the preliminary system design review, an extensive safety management plan addressing both the electrolyzer system and manufacturing area, where the system will be fabricated and tested, has been completed by Parker.

Conclusions and Future Directions

Significant progress has been made in DSM™ development. GES has demonstrated membrane reproducibility and durability as well as a significant improvement in electrolyzer cell efficiency. In addition, development efforts conducted under this project have

resulted in the reduction in the cost of the moderate-pressure PEM-based electrolyzer systems, an increase in the life of the low-cost cell-separators, and improved BOP components efficiency. The future objectives are to:

- Continue development of low-cost, high-efficiency membrane and cell-separator:
 - Scale-up of membrane and cell-separator to larger active areas (290 cm²).
- Complete electrolyzer stack and system preliminary designs.
- Fabricate a deliverable electrolyzer stack and system.
- Demonstrate prototype system at NREL.

FY 2009 Publications/Presentations

1. M. Hamdan, *Hydrogen Production Cost*. Hydrogen Production Cost Estimate Using Water Electrolysis Review Panel. Web Based Presentation – NREL. January 28, 2009.
2. M. Hamdan, *PEM Electrolyzer Incorporating an Advanced Low-Cost Membrane*. 2009 Hydrogen Annual Program Merit Review Meeting. Presentation #pd_21_hamdan, May 20, 2009.

References

1. Multi-Year Research, Development and Demonstration Plan. Hydrogen Production. DOE, Pg 3.1-14 <http://www1.eere.energy.gov/hydrogenandfuelcells/mypp/pdfs/production.pdf>.

II.E.4 Renewable Electrolysis Integrated System Development and Testing

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Subcontractors:

- Engineering Procurement & Construction, Denver, CO
- Spectrum Automation, Denver, CO
- Polyphotonics, Rochester, NY

Project Start Date: September, 2003
Project End Date: October, 2010

Objectives

- Explore system-level integration and optimization opportunities for renewable-energy-based electrolysis production facilities.
- Work closely with the electrolyzer industry to provide independent testing and validation of system performance of next generation electrolyzer systems awarded under DOE contracts, and provide feedback on potential areas for improvement.
- Quantify system-level efficiency improvements, system impacts, and cost reductions achieved by designing and building integrated power electronics to more closely couple varying energy from wind turbines and photovoltaic (PV) arrays to the electrolyzer stacks.
- Model, simulate, and optimize the renewable electrolysis system performance for dedicated hydrogen production for energy storage and electricity/hydrogen cogeneration.
- Evaluate the potential of using hydrogen as an energy storage mechanism to help integrate variable output renewable energy.
- Characterize and determine system impacts on commercial electrolyzer technology to accommodate the varying energy input from wind turbines and photovoltaics coupled directly to the hydrogen-producing electrolyzer stack.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (G) Capital Cost
- (H) System Efficiency
- (I) Grid Electricity Emissions (distributed)
- (J) Renewable Electricity Generation Integration (central)

Technical Targets

By addressing the technical barriers of integration with renewable energy sources, this project works to achieve the DOE cost targets for distributed and central electrolytic hydrogen production. One of the primary objectives of this work includes the development of integrated power electronics and control theory to couple renewable energy sources with the electrolyzer stack. This work will help reduce the capital cost and improve the efficiency to 68% (lower heating value, LHV) or 81% (higher heating value, HHV) of hydrogen production from the renewable electrolysis system by 2012.

- Distributed Electrolysis
 - By 2012, reduce the cost of distributed production of hydrogen from distributed electrolysis to \$3.70/gasoline gallon equivalent (gge) of H₂ (delivered) at the pump.
- Central Electrolysis
 - By 2012, reduce the capital cost of wind-coupled electrolyzer system to \$350/kW.
 - By 2012, reduce the cost of central production of hydrogen from wind electrolysis to \$3.10/gge of H₂ at the plant gate.

The 2012 electrolyzer capital costs assume a 12.5% savings on a standard H2A assumption for an advanced electrolyzer cost of \$400/kW [1].

Accomplishments

- Published major technical report on testing and findings of Wind-to-Hydrogen (Wind2H2) system operation.
- Developed and tested a 3rd generation power electronics package to integrate a variable-speed wind turbine to polymer electrolyte membrane (PEM) electrolyzer stack; measurements showed

- improved energy power transfer of about 17% over previous power electronics configurations.
- Performed analysis showing a 7% cost reduction in the cost of electrolytic hydrogen based on systems integration improvements of power electronics developed as part of the Wind2H2 project.
- Performed a wide array of comparison testing between the custom built direct current (DC)/DC power converter with maximum power point tracking (MPPT) and PV array directly connected to an electrolyzer stack.
 - For solar PV systems, NREL found that optimized MPPT power electronics delivered 10% to 20% more PV electricity to the electrolyzer stack compared to a direct connection.
- Published technical report on electrolyzer capital cost and efficiency improvement opportunities based on a worldwide survey of electrolyzer manufacturers.

Introduction

One issue that limits greater penetration of renewable energy sources (e.g., wind and solar) is their variable and seasonal energy production. One solution may be to produce hydrogen through water electrolysis and use that hydrogen in a fuel cell, either to fuel vehicles or to produce electricity during times of low power production or peak demand. Xcel Energy and the U.S. Department of Energy's (DOE) NREL have collaborated to design, install, and operate the Wind2H2 project, which demonstrates how to make hydrogen with renewable energy without producing greenhouse gases or other harmful by-products. The Wind2H2 project is helping researchers understand the hurdles and potential areas for improvement in emerging renewable electrolysis technologies. By allowing engineers to operate and configure an integrated electrolysis facility, this project has enabled the investigation and analysis of hydrogen production, compression, storage, and electricity generation that will provide valuable data, which can be used to improve the designs of future renewable electrolysis systems.

A significant focus of the Wind2H2 project is to explore system-level integration issues and opportunities for performance and cost improvements resulting from system-level optimization. NREL engineers are investigating how to maximize renewable energy use and optimize energy transfer within the Wind2H2 system. Most electrolyzers commercially available today are designed for grid-connected operation; therefore, they incorporate power electronics to convert alternating current (AC) from the grid to DC power required by

the cell stack. These power converters can represent 14% to 22% of the total cost of the electrolyzer. Power converters are also required for the renewable energy source. For example, when variable-speed wind turbines use wind energy they rely on power electronics to convert the variable frequency, variable voltage that is produced by the turbine to DC, which must then be converted back to AC for connection to the electric grid. By designing and incorporating dedicated power electronics packages that allow wind turbines to be more closely coupled to electrolyzer stacks, energy transfer within the system can be improved and costs lowered.

Approach

This project examines the design and optimization of electrolyzers, power electronics, and system components to integrate renewables and electrolyzers to improve the efficiency, cost, and robustness of these systems. Hydrogen production via electrolysis is heavily dependent on the cost of electricity. System integration research aims to reduce the cost of hydrogen production by:

- Exploring system-level integration and optimization opportunities for renewable-energy-based electrolysis production facilities.
- Quantifying system-level efficiency improvements, system impacts, and cost reductions achieved by designing and building integrated power electronics to more closely couple varying energy from wind turbines and PV arrays to the electrolyzer stacks.
- Gaining operational experience of a hydrogen production facility, evaluating appropriate safety systems and system controls for safe unattended operation, and identifying areas for cost and efficiency improvements.
- Evaluating the potential of using hydrogen as an energy storage mechanism to help integrate variable output renewable energy.
- Developing and optimizing advanced controls, subsystems, and power electronics to reduce electrolyzer capital cost and improve system efficiency.

Results

Experimental Findings

Efficiency Measurements: Electrolyzer system efficiency varies based on stack current and was measured for both the PEM and alkaline electrolyzer technologies (Table 1). The Wind2H2 Project found PEM electrolyzers more efficient than alkaline electrolyzers, contrary to expectations. At full stack current, the PEM electrolyzer had a system efficiency of 48% LHV (57% HHV). At the rated stack current, the alkaline system efficiency was found to be 35% LHV (41% HHV). Worth noting, the

measured hydrogen flow from the alkaline electrolyzer was 20% lower than the manufacturer's specifications. If the full hydrogen flow was measured, the alkaline system efficiency would have reached 50% (HHV).

TABLE 1. Electrolyzer System and Stack Efficiency

Efficiency	PEM Electrolyzer		Alkaline Electrolyzer	
	LHV	HHV	LHV	HHV
Stack Efficiency				
Low Current	80% (5 A)	95% (5 A)	78% (30 A)	92% (30 A)
Rated Current	63% (135 A)	75% (135 A)	59% (220 A)	70% (220 A)
System Efficiency				
Low Current	0% (15 A)	0% (15 A)	0% (35 A)	0% (35 A)
Rated Current	49% (135 A)	57% (135 A)	35% (220 A)	41% (220 A)

LHV – lower heating value; A – amps

Energy Transfer Optimization: NREL engineers have been investigating how to maximize renewable energy use and optimize energy transfer within the Wind2H2 system by designing and incorporating dedicated power electronics packages between the renewable electricity source and hydrogen-producing stacks of commercially available electrolyzer systems. Testing of these dedicated power electronics packages has shown improved energy transfer compared to non-optimized systems.

Wind Energy Optimization: NREL improved the energy transfer within wind-turbine-based renewable energy system and tested an AC/DC power electronics converter between a 10 kW wind turbine and 6 kW PEM electrolyzer stack. The test results of Figure 1 show about a 17% improvement over the Gen2 (yellow line) to the latest data (★) of the Gen3 design.

Solar (PV) Energy Optimization: NREL investigated energy transfer from a renewable energy

solar PV array, comparing a direct-connect from the PV array to the electrolyzer stack with a connection through an MPPT power electronics package designed at NREL. Measurements showed that in all cases, the system employing MPPT electronics captured 10% to 20% more energy than the direct-connect configuration (Figure 2).

Analysis

Based on the system-level optimization investigations conducted with the Wind2H2 system, NREL engineers estimated that optimizing power electronics in large-scale wind-based renewable electrolysis systems could reduce the cost of wind-to-hydrogen production from \$6.25/kg to \$5.83/kg. This 7% reduction in cost per kg of hydrogen is based on a capital cost improvement by eliminating the inverter from the wind turbine and the AC/DC power electronics in the electrolyzer and replacing them with a DC/DC converter between a wind turbine and electrolyzer stack. System-level integration of renewable energy sources and electrolyzer stacks can improve energy transfer within the system, increasing system efficiency and lowering overall cost of production.

This cost reduction analysis is based on the findings of an electrolyzer capital cost reduction investigation conducted by NREL. From a worldwide survey of electrolyzer manufacturers, NREL found that power electronics subsystems account for 14% to 22% of total electrolyzer system cost, and improvements in power electronics subsystems hold the second highest potential for lowering the cost of hydrogen produced via electrolysis, next to improvements in the electrolyzer stacks themselves. This research indicates that along with continued research into improving stack cost and performance, research and development efforts on power electronics subsystems can yield significant gains in overall electrolyzer system performance and cost.

FIGURE 1. Energy Transfer Improvements from 3rd Generation of the Wind Turbine Power Electronics Converter

FIGURE 2. Energy Transfer Improvements for MPPT Power Electronics over Direct Connect for 5 kW PV Array to PEM Electrolyzer Systems

Conclusions and Future Directions

The project is relevant to the DOE targets by addressing capital cost, efficiency, and renewable energy source integration to reduce the cost per kg of hydrogen. The approach includes demonstrating advanced controls, system-level improvements, and integration of renewable energy sources to commercially available electrolyzer stacks via NREL-designed-and-built power electronic controllers. Testing and characterization of power electronics packages and algorithms developed at NREL showed significant improvements in energy transfer within the system. Based on this work, NREL estimated that system-level optimization of power electronics subsystems alone could reduce the cost of wind-based hydrogen production by 7%.

NREL will continue to work to transfer technology and foster collaborative relationships with industry. This work will enhance the existing active and informal partnerships with industry, academia, and domestic/international researchers.

Additionally, NREL will complete the following:

- Modeling and analyzing cost and performance of future, large-scale renewable electrolysis systems based on lessons learned from Wind2H2 experimentation.
- Testing and characterizing the 3rd generation 10 kW wind turbine to electrolyzer stack power electronics.
- Testing and characterizing upgraded PEM electrolyzer (1.5 stack) configuration with direct and MPPT power electronics.
- Measuring 33 kW alkaline electrolyzer performance when provided a stack current proportional to the power signal from a 100 kW wind turbine.
- Verifying automated operation of the Wind2H2 system and conducting subsequent longer duration system testing and characterization.
- Testing and validating electrolyzer systems from DOE-sponsored projects.

FY 2009 Publications/Presentations

1. Harrison, K.W.; Martin, G.D.; Ramsden, T.G.; Kramer, W.E.; Novachek, F.J. (2009). Wind-To-Hydrogen Project: Operational Experience, Performance Testing, and Systems Integration. 95 pp.; NREL Report No. TP-550-44082.
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3. Harrison, K.; Martin, G.; Ramsden, T.; Saur, G. Renewable Electrolysis Integrated System Development and Testing – 2009 Hydrogen Merit Review Poster; NREL Report No. PO-560-45678.

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5. Harrison, K.W. “Wind to Hydrogen Demonstration Project.” Presented at the National Hydrogen Association 2009 Conference, Columbia, SC. April 1, 2009.

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II.F.1 Solar Cadmium Hydrogen Production Cycle

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Contract Number: DE-AC04-94AL-85000

Project Start Date: June 25, 2003
Projected End Date: August 31, 2009

Objectives

To demonstrate the technical feasibility and determine the economics of a solar cadmium hydrogen cycle. This includes:

- Validate the key reaction steps within the cadmium hydrogen cycle with experiments.
- Establish design concepts for process equipment based on experimental data.
- Integrate design concepts and solar plant and create a solar hydrogen plant flowsheet to calculate the process thermal efficiency and hydrogen cost.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section of the Hydrogen, Fuel Cells and Infrastructure Technologies (HFCIT) Program Multi-Year Research, Development and Demonstration (RD&D) Plan:

- (U) High-Temperature Thermochemical Technology
- (V) High-Temperature Robust Materials
- (X) Coupling Concentrated Solar Energy and Thermochemical Cycles

Technical Targets

This project is directed at demonstrating the feasibility of large-scale hydrogen production using a solar cadmium cycle. If successful, the project will address the following DOE cost and efficiency targets as outlined in the HFCIT Multi-Year RD&D Plan:

DOE Cost and Efficiency Targets for Hydrogen Production

Metric	Unit	2008	2012	2017
H ₂ cost	\$/kg H ₂	10.00	6.00	3.00
Efficiency (LHV)	%	25	30	>35

LHV-Lower heating value

Accomplishments

Experimental, design and modeling work has been carried out to determine the technical feasibility and financial viability of the cadmium solar hydrogen cycle with the following accomplishments:

- Established the effect of carrier gas and process parameters on cadmium oxide decomposition kinetics.
- Demonstrated sub 1,150°C cadmium oxide decomposition.
- Measured the cadmium-oxygen reaction rate with respect to temperatures and O₂ concentrations.
- Demonstrated means to use either molten or solid cadmium to generate H₂.
- Completed the process flowsheet and solar field design.
- Calculated H₂ cost using H2A.

Introduction

Preliminary flowsheet evaluation of the cadmium solar thermochemical hydrogen cycle has shown thermal efficiencies of nearly 70% (59% LHV). This process has the potential to supply low-cost hydrogen produced with a renewable energy source. In this cycle cadmium oxide is decomposed using concentrated solar heat at elevated temperatures. The decomposed cadmium vapor is then rapidly quenched to form molten cadmium in order to minimize the back reaction with oxygen. Hydrogen is generated in the third step of the cycle via either solid or molten cadmium hydrolysis.

This project's first goal is to carry out feasibility demonstrations of the three process steps in the laboratory. The resulting experimental data was used to generate design concepts for large-scale production process equipment. These concepts were then incorporated into a process flowsheet with a solar plant so that the thermal efficiency and cost of hydrogen can be derived. This provides an assessment whether a solar cadmium cycle can meet DOE's cost and efficiency targets.

Approach

Cadmium oxide decomposition was studied using thermogravimetric analysis (TGA). The effect of carrier gas on the decomposition temperature and rate were determined. In addition, the heating rate and experiment set up geometry were varied in order to understand the interplay between kinetics and process parameters [1].

To determine the feasibility of quenching decomposed cadmium vapor into molten cadmium, one needs to establish the required quench rate which in turn is controlled by the back reaction rate between cadmium vapor and oxygen. To measure this reaction rate, cadmium vapor was generated through molten cadmium evaporation. The vapor was then mixed with Ar gas containing oxygen at various concentrations. The gases flowed through a constant temperature zone at temperatures between 700°C and 1,400°C and were quenched upon exiting the furnace. The cadmium-oxygen reaction rate was then calculated based on the cadmium evaporation rate, reduction in oxygen concentration and the time of flight.

Cadmium hydrolysis can be carried out using either solid or molten cadmium. Both options had been investigated and it was found that molten cadmium hydrolysis has faster kinetics. Experiments were conducted to explore means to increase steam-cadmium contact. The goal is to provide inputs to equipment designs for maximum hydrogen generation. Data from all experiments were used to establish design concepts for large-scale process equipment. A flowsheet was then developed to determine the thermal efficiency and the hydrogen cost was calculated using H2A.

Results

TGA experiments were carried out to identify processing parameters that can reduce the cadmium oxide decomposition temperature. This is because the solar plant makes up approximately two-thirds of the cost of hydrogen. Experimental results showed that an

inert carrier gas, in particular helium, helps to reduce the decomposition temperature which stems from an increase in decomposition kinetics. Furthermore, by increasing the residence time of the CdO particle in the heated zone, the decomposition temperature can be reduced. Finally, enhanced oxygen diffusion kinetics also leads to a reduction in decomposition temperature. Figure 1 shows the cadmium oxide decomposition rate with respect to temperature under various carrier gases. The faster decomposition kinetics in helium, compared to an inert gas such as argon or CO₂, has to do with the higher diffusion rate of oxygen away from the decomposition interface in helium. The presence of oxygen leads to an increase in the decomposition temperature as expected, which is a result of the back reaction between cadmium and oxygen. Hence, an inert or reduced atmosphere environment will help to lower the decomposition temperature. The lowest decomposition completion temperature using the TGA was 1,140°C and it was accomplished using a low furnace heating rate. Based on the collected data, a cadmium oxide decomposer design concept was established. It is based on a fluidized bed which will enhance the heat and mass diffusion and increase particle residence time when compared to a flow through reactor. A schematic of this design concept is shown in Figure 2. This concept can be adapted to either a beam-down or beam-up tower.

The cadmium-oxygen reaction experiment results showed that the reaction rate was between 1%-6% of cadmium reacted per second for temperatures between 800-1,450°C. The oxygen concentration was between 1% to 20%. Most of the measured rates fall between 2%-3%. Modeling of the measurement results showed that the reaction rate has no dependence on oxygen concentration and is only slightly dependent on cadmium concentration. From the reaction rate data, the quenching of cadmium vapor into molten form

FIGURE 1. Decomposition rate of cadmium oxide as a function of temperature under various carrier gases. There are three regimes: i) helium, ii) argon and carbon dioxide and iii) air and pure oxygen.

FIGURE 2. Design concept of a windowed cadmium oxide decomposer integrated with molten cadmium quenching of decomposed cadmium vapor. This design works with a reflector-down tower. Secondary concentrators are located at the entrance to the decomposer.

will need to be completed in the order of one second so the majority of molten cadmium can be retained for hydrolysis to generate hydrogen. The baseline concept is to use fine molten droplets as the quench medium. With this approach, cadmium vapor can condense on the droplets instead of homogeneously nucleating from the super cooled gas. This will minimize the total cadmium surface area available for reaction with oxygen. Single droplet modeling of the molten cadmium quenching process is ongoing. This will provide an indication as to whether quenching using molten cadmium will be practical. The baseline concept is to integrate vapor quenching at the exit of the cadmium oxide decomposer as shown in Figure 2.

For the hydrogen generation step, experimental work has shown that the optimal hydrolysis temperature is between 450°–480°C. Furthermore, the hydrogen production rate can be enhanced by increasing the contact between steam and molten cadmium. This was demonstrated in a rotary kiln reactor in which molten cadmium was being turned over to expose fresh surfaces for hydrolysis. It was also shown that by placing inert pellets inside the rotary kiln, one can increase the molten cadmium surface area, thus further increasing the hydrogen generation rate. A design concept for a large-scale rotary kiln has been made and is shown in Figure 3. The reaction is carried out at elevated pressure and hydrogen is separated from steam with the aid of a membrane. This eliminates the need to condense the steam for separation and waste the excess heat energy. These design concepts were incorporated into a flowsheet and the process thermal efficiency was determined to be 58% (LHV) which exceeds DOE's target. This baseline case uses air as the carrier gas. For the hydrogen cost calculation, a solar plant was designed. It is based on a reflector-down geometry so that the chemical operations are on the ground. A final hydrogen cost between \$3.74 and \$5.53 for the 2015 case was calculated using H2A. It has the potential to meet the DOE 2017 target of \$3.00/kg of hydrogen.

FIGURE 3. Design concept of a rotary kiln reactor for molten cadmium-steam reaction to produce hydrogen. Cadmium and steam flow in opposite direction. At the end of the reactor, solid cadmium oxide is expected, thus eliminating the need for solid-liquid separation.

FIGURE 4. Block diagram of a solar-cadmium hydrogen plant. Cadmium oxide decomposition and decomposed vapor quenching take place during on sun hours. Hydrogen and electricity generation take place around the clock.

Figure 4 shows a simplified block diagram of the flowsheet for the hydrogen plant.

Conclusions and Future Directions

Key process steps of the cadmium solar hydrogen cycle have been demonstrated. Design concepts for a cadmium oxide decomposer and molten cadmium hydrolyzer have been established. The process efficiency and hydrogen cost meets the DOE 2012 target. In order to complete the feasibility study and to collect data for a future scale-up demonstration, the following work is recommended:

- Study the effect of quench rate on Cd-O₂ recombination.
- Measure the molten cadmium–oxygen reaction rate with a simulated bed quench set up.

- Conduct CdO decomposer prototype testing using a simulated solar source in order to better understand fluidization and materials handling issues.
- Conduct molten cadmium hydrolysis under pressure.
- Design a flowsheet based on a closed system using helium as carrier gas and calculate the hydrogen cost.

FY 2009 Publications/Presentations

1. “Solar Production of Hydrogen Using a Cadmium Based Thermochemical Cycle,” AIChE Fall Meeting, Philadelphia, November 16–19, 2008.
2. “Solar Production of Hydrogen Using a Cadmium Based Thermochemical Cycle,” NHA, March 29 through April 1, 2009.
3. DOE Annual Hydrogen Program Merit Review FY 2009, May 5–8, 2009.

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1. Galwey, A.K., Brown, M.E., *Thermal Decomposition of Ionic Solids*. Amsterdam, Elsevier Science B.V. 1999.

II.F.2 Solar High-Temperature Water-Splitting Cycle with Quantum Boost

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Subcontractors:

- University of Central Florida,
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- Electrosynthesis Co., Inc., Lancaster, NY

Project Start Date: September 1, 2007

Project End Date: August 31, 2011

Objectives

- Conduct technoeconomic analysis of photo/thermo-chemical water splitting cycles that can employ, advantageously, solar resource for the production of hydrogen.
- Select a cycle that has the best potential for cost-effective production of hydrogen from water and meeting the 2017 DOE target of \$3.00/gge at the plant gate (\$4.00/gge delivered).
- Demonstrate technical feasibility of the selected cycle in bench-scale.
- Show pre-commercial feasibility through economic analysis of the selected cycle and demonstration of a fully-integrated pilot-scale solar hydrogen production system.
- Perform techno-economic analysis of the selected cycle having a production capacity of 100 metric ton of hydrogen per day.

Technical Barriers

This project addresses the following technical barriers from the Production section (3.1.4) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (U) High-Temperature Thermochemical Technology
- (V) High-Temperature Robust Materials
- (W) Concentrated Solar Energy Capital Cost
- (X) Coupling Concentrated Solar Energy and Thermochemical Cycles

Technical Targets

Table 1 presents the progress made, to date, in achieving the DOE technical targets as outlined in the §3.1.4 Multi-Year Research, Development and Demonstration Plan – Planned Program Activities for 2005-2017 (updated Oct. 2007 version), Table 3.1.9: Solar-Driven, Thermo-chemical High-Temperature Thermochemical Hydrogen Production.

TABLE 1. Progress towards Meeting Technical Targets for Solar-Driven High-Temperature Thermochemical Hydrogen Production

Characteristics	Units	U.S. DOE Targets			Project Status
		2008	2012	2017	
Solar-Driven High-Temperature TCWSC Hydrogen Production Cost	\$/gge H ₂	10.00	6.00	3.00	5.73 ^a
Heliostat Capital Cost (installed cost)	\$/m ²	180	140	80	105
Process Energy Efficiency ^b	%	25	30	>35	25.82 ^c

^a Based on revised TIA reviewed H2A analysis of the photocatalytic sulfur-ammonia (SA) cycle (with dedicated photoreactor field).

^b Plant energy efficiency is defined as the energy of the hydrogen produced (lower heating value) divided by the sum of the energy delivered by the solar concentrator system plus any other net energy required for the process.

^c Electrolytic SA cycle efficiency is based on the most recent Aspen flow sheet analysis – see “Economic Analysis” section of the report.

TCWSC - thermochemical water splitting cycle; gge – gasoline gallon equivalent

Accomplishments

- Completed evaluation of the photocatalytic SA hydrogen production cycle and determined that the cycle enjoys high efficiency. However, further improvements in the technology and substantial component cost reductions are needed in order for the photocatalytic SA cycle to achieve the DOE long-term production cost target of \$3.00/kg of hydrogen.

- Initiated work on a new modification to the SA cycle that replaced photocatalytic process with an electrolytic one to conduct ammonium sulfite oxidation reaction.
- Identified an alternative sub-cycle to zinc sulfate/ZnO sub-cycle for oxygen production that is based on the all-liquid $K_2SO_4/K_2S_2O_7$ chemistry. Began study of associated reactions. This all-liquid sub-cycle will have a maximum temperature of less than 550°C if the relatively minor power required for the SO_3 decomposition to SO_2 is provided by on-site generated power.
- Fabricated a half-scale prototype glass-reinforced concrete (GRC) heliostat to demonstrate fabrication and design features for a full-scale system.
- Refined the AspenTM flowsheet of the SA cycle with the $K_2SO_4/K_2S_2O_7$ replacing $ZnSO_4/ZnO$ sub-cycle for oxygen production and an electrolytic process replacing the photocatalytic step for hydrogen generation.
- Determined hydrogen production costs of \$5.31/kg for the photocatalytic SA cycle with $ZnSO_4/ZnO$ sub-cycle.

Introduction

A limitation of most solar thermochemical cycles proposed for water splitting is that they do not take advantage of the unique characteristics of the solar resource. For example, the spectrum of sun light contains ultraviolet and visible photons that are very energetic and able to trigger photocatalytic reactions. Most solar thermochemical cycles ignore the potential of these photons and use their energy only as heat to drive thermochemical reactions. In the photocatalytic SA cycle, the photonic portion of solar spectrum is used directly to accomplish the hydrogen evolution step of the cycle. This means that less exergy is needed in the high-temperature oxygen production part of the cycle leading to comparatively lower operating temperatures and reduced requirements on the heliostat field and its associated costs.

Many thermochemical water splitting cycles, studied to date, have difficult and/or costly product separation steps, and materials handling and safety challenges. An example of the former is the Zn/ZnO cycle that requires rapid quenching of the high-temperature Zn-O₂ mixture to prevent unwanted back-reaction to ZnO. An example of later is the Cd/CdO cycle that involves handling and processing of toxic cadmium metal at high temperatures. On the other hand, the sulfur-ammonia cycle has potential to circumvent these and other shortcomings of the legacy thermochemical water splitting cycles while meeting the DOE hydrogen production cost targets.

Approach

To achieve the project objectives, the Bowman-Westinghouse “sulfur-family”, hybrid thermochemical water splitting cycle (“Hybrid Sulfur, HyS” cycle) was selected and modified by introducing ammonia as working reagent (thus sulfur-ammonia, SA, cycle) to attain more efficient solar interface and less problematic chemical separation steps. Several versions of the SA cycle were developed and evaluated – experimentally as well as analytically (using AspenPlusTM chemical process simulator).

Two approaches were considered for the hydrogen production step of the SA cycle, namely: photocatalytic and electrolytic oxidation of ammonium sulfite to ammonium sulfate in an aqueous solution. Also, two sub-cycles were evaluated for the oxygen evolution side of the SA cycle, namely: zinc sulfate/zinc oxide and potassium sulfate/potassium pyrosulfate sub-cycles. The laboratory testing and optimization of all the process steps for each version of the SA cycle were then carried out. Once the optimum configuration of the SA cycle has been identified and cycle validated in closed loop operation in the lab, it will be scaled up and on-sun tested.

Results

Cycle Evaluation and Analysis

The first version of the SA cycle employed a photocatalytic reaction step for generating hydrogen and a zinc sulfate/zinc oxide sub-cycle for oxygen generation. The SA cycle also provided an option to split the solar spectrum so that shorter wavelength photons could be diverted to the photocatalytic reactors while lower-energy, longer-wavelength solar heat (>520 nm) redirected to power and drive the oxygen production reactions. Reactions involved in the photocatalytic SA cycle are given below:

The photocatalytic step (2) occurs at near ambient temperatures under one sun irradiation. Therefore, photoreactors can be inexpensive and made from low-cost materials. The oxygen production step (4) provides facile separation of O₂ from SO₂ and water vapor. Reactions (3) and (4) form a sub-cycle by which ZnO is reacted with ammonium sulfate, in the low temperature reactor, to form zinc sulfate that is fed to the high

temperature reactor wherein it is decomposed to SO_2 , O_2 and ZnO . Zinc oxide is returned to the low-temperature reactor – closing the sub-cycle. The net cycle reaction (represented by reactions 1-4) is decomposition of water to form hydrogen and oxygen. All of the reaction steps described above have been demonstrated in the laboratory and shown to occur without undesirable side reactions.

In the course of Fiscal Year 2008 activities, it was shown that the most active co-catalysts for conducting the hydrogen production step were noble metals (*e.g.* Pt, Pd, Ru, Rh, Ag, and Au) and transition-metal oxides like NiO promote H_2 evolution. Among noble metal promoters, Pt is the most efficient and often used for photocatalytic H_2 production. We have prepared a novel and highly efficient CdS -supported $\text{Pd-Cr}_2\text{O}_3$ nano-composite co-catalyst. To determine the relative activity of $\text{Pd-Cr}_2\text{O}_3/\text{CdS}$ in relation to Pt/CdS , CdS was doped with 0.5 wt% of Pt (Pt/CdS) and its photocatalytic activity was measured under the same experimental conditions as those employed for evaluating $\text{Pd-Cr}_2\text{O}_3/\text{CdS}$. Figure 1 depicts results obtained for the hydrogen evolution rate of $\text{Pd-Cr}_2\text{O}_3/\text{CdS}$ photocatalyst and that of Pt/CdS . The data reveal that doping CdS with $\text{Pd-Cr}_2\text{O}_3$ co-catalyst is as effective as and a less expensive alternative to Pt doping of CdS for photocatalytic production of hydrogen from ammonium sulfite.

Based on the AspenTM chemical process simulation of the photocatalytic-SA cycle, splitting the solar spectrum leads to reasonably high solar-to-hydrogen energy conversion efficiencies. However, these optical

losses mean a larger heliostat field is needed in order to conduct heat driven higher temperature oxygen production sub-cycle. Moreover, the present cost of the dichroic mirrors needed for beam splitting is quite high. Both these aspects lead to higher hydrogen production costs. On the other hand, if a dual field configuration is used so that the photocatalytic and thermolytic processes utilize physically separate heliostat fields, the overall costs are lower, but the solar-to-hydrogen energy conversion efficiency will be low.

At the October 2008 Solar Thermochemical Hydrogen (STCH) Production team meeting held at the DOE Golden Field Office and the January 2009 Technical Team Review meeting at University of Nevada, Las Vegas that followed, we were instructed to consider electro-oxidation, rather than photocatalytic oxidation, of aqueous ammonium sulfite solutions as the hydrogen production step of the SA cycle. The rationale for this was that substituting an electrolytic step for the photocatalytic step may produce a hydrogen production process that is more efficient, has lower overall cost, and higher likelihood of meeting U.S. DOE cost and efficiency targets for solar thermochemical hydrogen production (see Table 1).

In order to accelerate development of a viable electrolytic process for oxidation of aqueous ammonium sulfite to ammonium sulfate, we added a new team member experienced and highly skilled electrochemical company – Electrosynthesis Company (ESC), Inc. Figure 2 depicts a simple mass and energy flow diagram of the proposed electrolytic SA cycle.

FIGURE 1. Hydrogen evolution vs. time for metal doped cadmium sulfide (CdS) photocatalysts – CdS loading: 1.67 g/L of 1.0 M $(\text{NH}_4)_2\text{SO}_3$; size of photoreactor window (A_w) = 122.7 cm^2 ; irradiance ($\Delta\lambda = 300\text{-}500\text{ nm}$) $I_{\Delta\lambda} = 294.4\text{ W/m}^2$; $\eta = (\text{H}_2\text{ evolution rate} \times \text{lower heating value of H}_2)/(\text{A}_w \times I_{\Delta\lambda})$.

Electro-Oxidation of Aqueous Ammonium Sulfite Solutions

Parallel experiments were conducted at FSEC and ESC to determine the optimum process conditions for the electro-oxidation of aqueous ammonium sulfite to ammonium sulfate and hydrogen. Experiments conducted at ESC employed a membrane electrode assembly (MEA) composed of a cast NRE212 membrane coated on one side with fine platinum particles at Pt loading of about 100 $\mu\text{g}/\text{cm}^2$. In an effort to minimize the anode overpotential, the gap between current collector and membrane was reduced to about 1 mm with about 3 mm of felt in the flow space. The flow frames were filled with felt to support the current collectors and provide sufficient contact between the current collectors and active components. The active surface area of the ESC cell was 10 cm^2 . Anolyte was 250 mL of 2 M $(\text{NH}_4)_2\text{SO}_3$ (pH of 8.3) and catholyte consisted of 250 mL of deionized water adjusted to a pH of 9.8 using NH_4OH .

Figure 3 depicts the current-voltage (I-V) curve obtained for the ESC cell at 80°C. The cell voltage for this experiment was about 200 mV lower than an

FIGURE 2. Schematic Representation of the Electrolytic SA Cycle

identical cell with anode side MEA platinum loading of $2 \mu\text{g}/\text{cm}^2$ implying that higher Pt loading is beneficial to reducing cell potential. The rate of H_2 production for this test was $23.0 \pm 0.1 \text{ mL}/\text{min}$ indicating a cell current efficiency of 100% – note that the theoretical H_2 production rate at 3 A cell current is 22.8 mL/min.

At the high current density and high temperatures, the cathode reaction was quantitative with respect to hydrogen formation. However, when run occurred at low current density that resulted in a lower hydrogen production efficiency. The data obtained at the ESC seem to imply that for higher performance, it is more advantageous to operate the cell at high temperatures in order to lower the cell potential.

The decomposition of ammonium sulfite to ammonia, SO_2 and water at high cell operating

FIGURE 3. Variation of cell voltage, anolyte pH and catholyte pH vs. time for the ESC test cell V (graphite felt divider anode, GFD3, provided by SGL-Carbon Group, NRE212 membrane, MEA cathode with $\sim 100 \mu\text{g}$ Pt/ cm^2 , grooved graphite current collectors) operating at 80°C and fixed current density of $300 \text{ mA}/\text{cm}^2$.

temperatures does not represent a loss in efficiency (this occurs regardless of whether the electrode is polarized or not) and can be recovered by scrubbing the decomposition gases into ammonium bisulfite solution at room temperature and recovered and returned to the anolyte.

Ammonia is stripped from ammonium hydroxide at higher temperatures but this can be suppressed by elevating the cell operating pressure. Ammonia can also be scrubbed back into the anolyte to prevent its pH from dropping excessively (see Figure 3). Keeping the ammonia concentration low has the added benefit of decreasing the overpotential on the cathode.

Furthermore, the flow sheet analysis of the electrolytic SA cycle has shown that the energy needed to operate the electrolysis plant can be generated on-site using waste heat to produce steam. The electrolytic system can operate 24/7 and requires a much smaller footprint than does the photocatalytic process.

Another issue that came up at the October 2008 STCH team meeting held at DOE Golden Field Office related to design of the high temperature reactors that make up the SA cycle's O_2 production sub-cycle and solids handling and transport from one reactor to the other. In order to address this concern, we modified the processes involved in the oxygen production sub-cycle of the SA cycle and replaced them with all liquid processes described in the following.

Aspen™ Flow Sheet of the Electrolytic SA Cycle with $\text{K}_2\text{SO}_4/\text{K}_2\text{S}_2\text{O}_7$ Sub-Cycle

The high-temperature reactions of the electrolytic SA cycle can be modified to allow an all fluid materials transport instead of having to handle solid reagents. The new chemistry replaces earlier reactions (3) and (4) with the following reactions:

The advantages of the new sub-cycle are, among others:

Simplified material handling – The liquid $\text{K}_2\text{SO}_4/\text{K}_2\text{S}_2\text{O}_7$ mixture can be pumped through pipes rather than bucket lifting and/or conveyor transport needed for the earlier ZnO/ZnSO_4 sub-cycle.

Lower temperature step – Reaction (5) is carried out at 400°C which is readily available by employing parabolic trough solar concentrating technology. This can result in more efficient and cost-effective operation as compared to the power tower approach.

Simplified thermal storage and energy recovery – Storage of and energy recovery from the liquid $K_2SO_4/K_2S_2O_7$ system can be achieved via existing technology and does not require complex and elaborate engineering and construction.

The most recent Aspen™ flow sheet of the electrolytic SA cycle with all liquid $K_2SO_4/K_2S_2O_7$ sub-cycle developed at FSEC is shown in Figure 4. Hydrogen is produced at a rate of 5,556 kg/hr based on 24 hr/day operation in the ELECTROL electrolysis reactor according to reaction (2). The reactor is operated at 2 bar pressure. Theoretical power input to the electrolyzer is 96 MW (based on an experimental cell running at 94°C, 0.65 V cell potential and current density of 70.4 mA/cm² with 100% current efficiency). The hydrogen gas is separated from steam in a flash unit FL-H2 and compressed to produce 5,556 kg/hr H₂ with molar purity of 98% at 21.7 bar.

The aqueous ammonium sulfate solution produced in ELECTROL passes through a series of heat exchangers for preheating prior to entering the solar thermal reactor LOTEMRXN which performs reaction (5). Hot product gases from this reactor (NH₃

and H₂O) are easily separated from molten salt $K_2S_2O_7$ and expanded in a turbine (TURBINE1) to produce electricity. These gases are condensed in TOWER 2 (simulating a condensing turbine), mixed with recycled and makeup water, and fed to SFIT-GEN reactor where reaction (1) occurs. The molten $K_2S_2O_7$ exiting the LOTEMRXN is converted to gaseous and liquid products via reaction (6) that is carried out at 550°C (represented in the Aspen™ flow sheet by a second reactor MIDTEMRX).

The product SO₃ gas from reaction (6) is preheated in HX-5 and fed to a third solar thermal reactor (represented by HITEMRXN), where reaction (7) is performed at 850-1000°C. The gaseous products from reaction (7) are used to preheat the incoming SO₃, compressed and fed to SFIT-GEN reactor. SO₂/O₂ and NH₃/H₂O streams are reacted exothermically according to reaction (1) to produce aqueous ammonium sulfite (NH₄)₂SO₃ solution and a gaseous H₂O/O₂ stream in SFIT-GEN. The solution generated by reaction (1) is fed back to the electrolytic reactor. The gaseous products are cooled and condensed via cooling tower (TOWER). Oxygen is released from the system (represented by flash FL-O2). Cooled water exiting FL-O2 is combined with NH₃/H₂O stream exiting TOWER2. The resulting stream is pumped into SFIT-GEN.

We note that: reaction (5) in LOTEMRXN reactor can be carried out in a parabolic trough type solar receiver/reactor. Reaction (6) in MIDTEMRX reactor

FIGURE 4. AspenPlus™ Flow Sheet for the Electrolytic SA Cycle with $K_2SO_4/K_2S_2O_7$ Sub-Cycle

can be performed in a series of tubes running through a power tower receiver. Reaction (7) that occurs in HITEMRXN reactor can be carried out in a bayonet type solar reactor operated in a power tower receiver. The ELECTROL reaction is still under development at ESC and FSEC. The SFIT-GEN reaction occurs spontaneously and evolves heat.

In this analysis, we used a ratio of 8 moles of H_2O per mole of $(\text{NH}_4)_2\text{SO}_3$. Lower ratios can be tolerated if the stream temperatures and pressures are adjusted to prevent precipitation of salt. The electrolyzer power requirement of 96.015 MW estimated from the laboratory data (for a two-dimensional cell operating at 94°C , Nafion[®] 211 membrane coated with 0.4 mg/cm^2 Pt and graphite current collectors) is close to the theoretical value calculated using Faraday's law with the cell potential of 0.65 V and hydrogen molar flow rate of 2,756 kmol/hr (for 24 hr around the clock electrolyzer operation). This is due to the fact that the cell current efficiency was essentially 100%.

The calculated efficiency of the electrolytic SA cycle (with $\text{K}_2\text{SO}_4/\text{K}_2\text{S}_2\text{O}_7$ sub-cycle) from the flow sheet depicted in Figure 4 was 18.7% (lower heating value). This calculation took account of the energy produced by TURBINE1 minus the energy needed to operate the electrolysis plant, compressors and pumps.

Solar Concentrator Configuration for Photocatalytic SA System

Several configurations were evaluated for the photocatalytic SA system. Beam-splitting systems were found to be more expensive due to the cost of beam-splitting mirrors and because the heliostat field needs to be 30-40% larger if beam splitting is used. The best configuration for a beam-splitting system was found to be a North-field heliostat field with full-spectrum mirrors, a "cold" mirror at the top of the tower that redirects the ultraviolet/visible light back down to the ground level, and a photoreactor field located south of the tower that receives about two suns worth of ultraviolet/visible (one from the sun and one from the reflected light from the cold mirror). This design maximized the solar efficiency of the photocatalytic SA system.

The most cost-effective photocatalytic SA system design was determined to be a system with a heliostat/power tower feeding energy to the high-temperature reactors, and a separate flat-plate photoreactor field. This was less "efficient" due to the land usage for the large flat-plate photoreactor field, but the cost was less due to having a smaller heliostat field and not needing beam-splitting mirrors.

Solar Field Optimization

In this year, the design of a heliostat field was further refined and evaluated. A computer model was built using hour-by-hour TMY3 weather data for Barstow, CA to generate annual performance estimates for the heliostat field. Using H2A and Sargent & Lundy cost data the capital cost for the heliostat field was developed and used to optimize the heliostat field for minimum energy cost. The optimum field was found to have a 90 m tower with about 68,000 m^2 of heliostats over a land area of 49 acres.

A conceptual design of a receiver configuration suitable for the SA cycle was developed. Approximately 1/3 of the thermal energy is needed at the highest temperature of approximately $800\text{--}850^\circ\text{C}$. Based on a square heliostat size of 10 m^2 , and using the actual sun size, an estimate of the potential concentration and image size from heliostats within the field was developed. For the high temperature reactor a rectangular aperture of 6 m by 6m was chosen to minimize the amount of optical spillage at the receiver. Similarly, for the lower temperature reactor, at 350°C , an aperture of 8.5 m by 8.5 m was selected. The reason for the larger aperture at the lower temperature is that the energy for that receiver would be delivered from the heliostats furthest from the tower, where beam spread is the greatest.

The solar field configuration is continuing to be updated as the thermochemical system evolves. The primary present activity is to incorporate the all-liquid $\text{K}_2\text{SO}_4/\text{K}_2\text{S}_2\text{O}_7$ system.

Heliostat Cost Reduction

The design of a GRC-based heliostat system has continued. A preliminary design was developed, and a half-scale prototype GRC heliostat has been fabricated and is being tested (see Figure 5). The purpose of the prototype was to develop and demonstrate fabrication techniques and design features for the full-scale system.

The design features a factory-cast heliostat structure with reinforcements and mounting provisions built-in, and a factory-cast foundation ring with integral azimuth drive features. The elevation drive is actuated with a linear actuator of the type used for satellite dishes. The azimuth drive uses a "spring-worm" drive design developed by SAIC several years ago, with the loops of a coil spring acting as the teeth of a ring gear. A prototype control system was developed using a microprocessor-based controller with solar photovoltaic power and wireless communication. Evaluation of the prototype will be completed, and a final design of a full-scale unit will be finished so that a production cost analysis can be completed.

FIGURE 5. SAIC GRC Heliostat Design

Economic Analysis

The photocatalytic SA process with separate heliostat and photoreactor fields was analyzed using the H2A economic model. The resulting cost for hydrogen was found to be \$5.73. The cost analysis of the electrolytic SA cycle is underway. The preliminary cost figures for the electrolysis plant have been determined. Tables 2 and 3 provide the basis for calculating the cell and module capital costs, respectively. The data in these tables have been estimated from recently published information for the HyS thermochemical hydrogen production cycle [1].

TABLE 2. Basis for Cell Capital Costs

Item	Description	Cost Basis	\$/m ²
Membrane	NRE212 or equiv	\$300/m ²	300
Gas diffusion layers	Porous carbon	\$75/m ² (2 layers)	150
Electrocatalyst	0.3 mg/cm ² Pt (total)	\$1,500/troy oz	150
Bipolar plates	3/8" graphite	\$200/m ²	200
Seals, gaskets, etc.	PEEK or equivalent	\$50/m ²	50
Cell assembly	Automated	1 man-hr at \$50/man-hr	50
Single cell cost			900

PEEK – Polyether ether ether ketone

Each module has been assumed to contain 230 cells (each incorporating a 1 m² of active area) to which the following cost items have been added:

Installed costs were calculated for the electrolysis plant of the SA cycle using cost assumptions of the Tables 2 and 3 for cell fabrication and applying TIAX

TABLE 3. Module Capital Costs

Item	Description	Cost Basis	\$/m ²
Cells	230 units	\$900/m ² (see Table 2)	900
End plates, tie rods, and other pressure comp.	Carbon steel	\$23,000	100
Current collectors and connection to direct current bus	Copper	\$9,200	40
Assembly	Off site	64 man-hr at \$50/man-hr	20
Overhead	Manufacturing	20% of materials and labor	192
Module Cost			1,252
Balance of Electrolyzer System (BOES) Contribution			648
Total Including BOES Contribution			1,900

installation factor of 1.2. The installed capital cost of the electrolytic plant of the SA cycle calculated based on the best laboratory test data obtained to date (for which the total required membrane area is approximately 209,800 m²) is estimated to be about \$204.4 per metric ton of hydrogen produced. Note that the electrolytic SA cycle generates 109 MW of power that is more than that needed to run the electrolysis plant (*i.e.*, 96.015 MW). Total on-site power consumption including that required for the compressors and pumps, is about 106.5 MW. Total power input into the high temperature SO₃ decomposition reactor is about 70.6 MW which is considerably less than that generated on-site.

Conclusions and Future Directions

In summary:

- The photocatalytic SA cycle has been shown to be technically feasible and able to achieve high efficiency. However, further improvements in the technology and substantial components cost reduction are necessary in order for the photocatalytic SA cycle to achieve the DOE cost target of \$3.00/kg of hydrogen produced by 2017.
- The electrolytic SA cycle is in early development stage, so further performance improvements and cost reductions are likely.
- Based on the work performed to date, it appears that the electrolytic SA cycle has potential to meet DOE's near- and long-term H₂ production cost and efficiency goals.
- GRC has promise to reduce heliostat cost substantially.

Activities planned for the upcoming year include:

- Completion of phase 1 activities.
- Documentation of the photocatalytic SA cycle results.
- Finalization of the thermal reactor/receiver design.
- Conclusion of the solar field configuration and design.

With respect to the electrolysis work, we note that both the anodic oxidation of sulfite and cathodic H₂ evolution reaction are pH dependent,

$$E^0 = +0.172 \text{ V/normal hydrogen electrode}$$

$$E^0 = 0.930 \text{ V/normal hydrogen electrode}$$

The main source of voltage loss is due to the anode losses. Therefore, future activities in this area will be focused on reducing the cell voltage by finding conditions that allow anode function at high pH without adverse effect on localized pH changes. One approach is to introduce some buffering capacity into the solution.

Future plans include additional work to:

- Identify catalysts that will reduce the over-potential at the anode and allow operation at high current densities.
- Complete the electrolytic hydrogen production and electrolytic cell optimization tests.
- Finalize the electrolytic SA cycle H2A analysis.

We should also note that there is some disagreement involving measurement of the rate of electrolytic hydrogen production performed at FSEC and ESC evidenced by differences in current density obtained by the cells at the respected laboratories. Efforts are underway to resolve measurement issues by testing and verifying ESC cell performance independently at FSEC.

Future activities involving the solar interface include:

- Recombine anolyte and catholyte streams to control and maintain fixed pH.
- Refine solar field and receiver design as the chemical plant needs evolve.
- Conduct detailed production cost estimate for GRC heliostat system based on prototype test results.
- Complete the design of a full-scale prototype of pre-commercial GRC heliostat design.

Finally, assuming a “GO” decision by the U.S. DOE, the next phase of the project will involve laboratory demonstration and validation of the closed-loop SA cycle followed by on-sun hydrogen production demonstration.

Special Recognitions & Awards/Patents Issued

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2. Huang, C., Yao, W., Muradov, N.Z., T-Raissi, A. “Non-Pt Based Pd-Cr₂O₃/CdS Photocatalysts for Solar Photocatalytic Hydrogen Production,” Provisional Patent filed March **2009**.

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1. Yao, W., Huang, C., Muradov, N.Z., T-Raissi, A. “Photocatalytic H₂ Evolution on Visible Light Illuminated CdS Supported Pd-Cr₂O₃ Nanocomposite Cocatalyst Using Regenerable Sacrificial Donor,” Paper submitted to the *J. of the American Chemical Society*.
2. Taylor, R. T-Raissi, A. Davenport, R. “Solar Hydrogen Production Through High-Efficiency Thermochemical Water Splitting with Photocatalytic or Electrolytic Steps,” *SOLAR 2009* (ASES National Solar Conference), Buffalo, NY, 11–16 May **2009**.
3. Taylor, R., Davenport, R., T-Raissi, A., Muradov N., Huang C., Fenton S., Block D. “Solar Hydrogen Production Through Thermochemical Water Splitting with Photocatalytic or Electrolytic Steps,” *National Hydrogen Association Conf. & Expo*, Columbia, South Carolina, April **2009**.
4. T-Raissi, A., Fenton, S. “H2A Analysis of the Photocatalytic Sulfur-Ammonia Cycle – Revised Analysis,” delivered to TIAX, March **2009**.
5. T-Raissi, A., Taylor, R., Davenport, R. Presentation at the *STCH Meeting*, University of Nevada at Las Vegas, January 22, **2009**.
6. Taylor, R., T-Raissi, A., Davenport, R. Presentation at the *STCH Meeting*, DOE Golden Field Office, October 8–9, **2008**.

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II.F.3 Solar-Thermal Hydrogen Production Using a Metal-Oxide Based Thermochemical Water Splitting Cycle

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Contract Number: DE-FG36-03GO13062

Project Start Date: June 1, 2005

Project End Date: September 30, 2010

Objectives

- Research and develop a cost-effective $\text{Mn}_2\text{O}_3/\text{MnO}$ and ferrite-based ($\text{M}_x\text{Fe}_y\text{O}_4$) solar-thermal thermochemical cycle through theoretical and experimental investigations.
- Develop a process flow diagram and carry out an economic analysis of the best process option.

Technical Barriers

This project addresses the following technical barriers from the High-Temperature Thermochemical, Solar-Driven Production of Hydrogen section (3.1.4) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (U) High-Temperature Thermochemical Technology
- (V) High-Temperature Robust Materials
- (W) Concentrated Solar Energy Capital Cost
- (X) Coupling Concentrated Solar Energy and Thermochemical Cycles

Technical Targets

Solar-Driven High-Temperature Thermochemical Hydrogen Production:

This project is conducting fundamental studies of metal oxide-based thermochemical cycles. Insights gained from these studies will be applied toward solar-driven high-temperature hydrogen production that meets the following DOE cost targets:

- 2012: \$6/gge H_2
- 2017: \$3/gge H_2

Accomplishments

- Fabricated a high surface area CoFe_2O_4 metal ferrite spinel using atomic layer deposition (ALD).
- Demonstrated water splitting capability with multiple cycles.

Introduction

The most benign and renewable method for obtaining hydrogen is by using sunlight to split water. Splitting water directly with solar-thermal energy is not practical since the temperature required in order to obtain high conversion is above 4,000 K. Another huge challenge is the requirement to separate gaseous hydrogen from oxygen at these temperatures. Multi-step thermochemical cycles which split water through a series of two or more chemical reactions provide an opportunity for carrying out the high step in the process at more modest temperatures of less than 2,000 K. In addition, they remove oxygen and hydrogen in separate steps, thus avoiding the recombination issues. The $\text{Mn}_2\text{O}_3/\text{MnO}$ and ferrite cycles allow lower operating temperatures than other thermochemical cycles and are of particular interest.

Approach

An alternative ferrite cycle in which the ferrite (CoFe_2O_4) is deposited on a porous Al_2O_3 support (30 m^2/g) via ALD has been developed. Rather than a traditional cycle, in which the ferrite is deposited on an inert support or is unsupported, the ferrite reacts with Al_2O_3 during thermal reduction to form hercynite (FeAl_2O_4). This is advantageous because the reaction between the ferrite and Al_2O_3 is favored at lower temperatures than the reduction of Fe^{3+} to Fe^{2+} on an inert support. Subsequent water oxidation is then achievable at 1,000°C, similar to other ferrite cycles [1,2]. This redox cycle is shown in the two step reaction:

Results

Thermodynamic Analysis

Thermodynamic modeling was performed using the thermodynamic software package FactSage. Recent advances by Allendorf et. al. have contributed to a greater understanding of ferrite thermodynamics, and the methods used in their paper were utilized in our analysis [3]. Thermodynamically, reduction of a ferrite on an Al_2O_3 support is favored at lower temperatures than on an inert support. Reduction is predicted to reach a maximum at 1,300°C for cobalt ferrite on alumina, whereas is expected to reach completion at 1,500°C for unsupported cobalt ferrite. Additionally, iron (II,III) oxide on alumina is reduced at 1,450°C but unsupported iron (II,III) oxide is not reduced fully at temperatures even greater than 1,600°C.

The subsequent hydrolysis reaction at 1,000°C for alumina supported cobalt ferrite is expected to produce more H_2 per gram of unsupported ferrite at lower reduction temperatures, as shown in Figure 1. Unsupported cobalt ferrite does not produce a significant quantity of H_2 until about 1,400°C, and begins to increase rapidly afterwards. However, supported cobalt ferrite produces nearly as much H_2 at 1,200°C as unsupported cobalt ferrite at 1,400°C. Nearly three times as much H_2 is expected to be evolved for alumina supported ferrite at a reduction temperature of 1,200°C.

Experimental Results

CoFe_2O_4 on Al_2O_3 (60% by mass, 30 m^2/g) was reduced at temperatures between 1,200°C and 1,500°C in

FIGURE 1. H_2 Evolution Profiles as a Function of Temperature for CoFe_2O_4 on Al_2O_3 and CoFe_2O_4

a high temperature horizontal furnace. A powder X-ray diffractometer (XRD, $\text{CuK}\alpha$ radiation, $\lambda = 1.5406\text{\AA}$) was then used to measure the crystallinity changes of the sample. Only peaks representative of Al_2O_3 are present for uncoated alumina substrates. However, once coated with CoFe_2O_4 , the alumina peaks are reduced and mostly only peaks due to CoFe_2O_4 are present. Only alumina's strongest peak, at 26.65 degrees, is apparent. At 1,200°C, peaks representative of FeAl_2O_4 and Al_2O_3 are present, and as the temperature is increased peaks due to FeAl_2O_4 become more pronounced and alumina peaks are diminished. This is likely due to the fact that the sample is reduced further at higher temperatures, resulting in an increased concentration of FeAl_2O_4 .

A comparison between O_2 evolution during the reduction of CoFe_2O_4 on Al_2O_3 (60% by mass) and on ZrO_2 (33% by mass) is shown in Figure 2. Oxygen begins to evolve slightly after the temperature reaches 800°C for CoFe_2O_4 on alumina, which agrees well with thermodynamic modeling discussed above. By 1,200°C, the reaction rate has reached a maximum, and O_2 subsequently decreases. This is in contrast to CoFe_2O_4 on zirconia, in which the oxygen begins to evolve once the temperature reaches 1,150°C.

Samples reduced at temperatures between 1,200°C and 1,500°C were oxidized at 1,000°C, and results are shown in Figure 3. The coprecipitated sample does not show any appreciable H_2 evolution until the reduction temperature reaches 1,400°C, which agrees well with thermodynamic calculations discussed above. However, at 1,200°C for CoFe_2O_4 on Al_2O_3 , there is a substantial amount of H_2 evolved, and it increases linearly with temperature. The amount of H_2 evolved at this temperature is greater than the coprecipitated sample reduced at 1,400°C.

Finally, samples were cycled at 1,200°C reduction and 1,000°C oxidation in order to study their cyclical repeatability, and results are shown in Figure 4. The

FIGURE 2. Comparison of O_2 Evolution Profiles during Reduction of CoFe_2O_4 on Al_2O_3 and ZrO_2

FIGURE 3. Comparison of H₂ Evolution as a Function of Reduction Temperature

FIGURE 4. Eight Cycles Conducted at 1,200°C Reduction and 1,000°C Oxidation

conversion varies between 15% and 18%, and there is no obvious increasing or decreasing trend. However, a more detailed cycling study should be conducted to determine the samples lifetime over many more cycles in order to study its efficacy for this water splitting cycle.

Conclusions and Future Directions

Significant theoretical/experimental progress has been made with the CoFe₂O₄ “ferrite” cycle:

- Thin films were produced by ALD.
- Alumina was demonstrated to be a unique substrate that can take part in the reaction cycle.
- The cycle was experimentally demonstrated.

Future work:

- Additional cycle validation via further cycling.
- Gain better understanding of H₂ generation and reduction kinetics.

FY 2009 Publications

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2. Y. Tamaura, A. Steinfeld, P. Kuhn, K. Ehrensberger, *Energy* **20/4** (1995) 325.
3. M.D. Allendorf, *Energy & Fuels* **22/6** (2008) 4115.

II.G.1 R&D Status for the Cu-Cl Thermochemical Cycle

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Start Date: June 2007

Projected End Date: September 2009

Objective

The strategic objective is to develop a robust process for producing hydrogen that meets DOE's targets for cost and energy usage; the tactical objective is to conduct experimental and modeling programs that will facilitate the development of an integrated laboratory scale demonstration for the Cu-Cl cycle that can operate with heat sources that provide process heat near 550°C.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (U) High-temperature Thermochemical Technology
- (V) High-Temperature Robust Materials
- (W) Concentrated Solar Energy Capital Cost

Technical Targets

The technical targets are the cost of hydrogen production and the process energy efficiency.

- For 2017, these are \$3.00 per gasoline gallon equivalent (gge) H_2 and >35% (lower heating value, LHV), respectively.

Accomplishments

- Developed a method/reactor design for obtaining high yields (near 100%) of the desired products in the hydrolysis reaction.
- Verified that 550°C was the maximum process temperature and showed that no catalysts were required for the thermal reactions.
- Completed a conceptual process design and Aspen flowsheet for the Cu-Cl cycle.
- Completed an estimate of the efficiency and cost of producing hydrogen based on the conceptual process design.
- Continued participation in an International Nuclear Energy Research Initiative (INERI) with the Atomic Energy of Canada Ltd. (AECL) and six Canadian universities and an informal information exchange with Commissariat à l'Énergie Atomique (CEA) in France.
- Continued participation in a Nuclear Energy Research Initiative-Consortium (NERI-C) with three U.S. universities.
- Identified promising membrane materials for the electrolyzer through the INERI and NERI-C programs; these have the potential to eliminate the copper crossover observed experimentally.

Introduction

The focus of the Nuclear Hydrogen Initiative (NHI) of the U.S. Department of Energy's Office of Nuclear Energy (DOE-NE) is to identify and ultimately commercialize hydrogen production technologies that are compatible with nuclear energy systems and that do not produce greenhouse gases. The NHI objective is to operate a nuclear hydrogen production plant at a cost competitive with other alternative transportation fuels by 2019. The NHI is currently supporting development of two sulfur cycles and high temperature steam electrolysis as well as the Cu-Cl cycle because of its lower temperature and potentially simpler unit operations. The U.S. Department of Energy's Office of Energy Efficiency and Renewable Energy (DOE-EERE) is also supporting the development of thermochemical cycles that use solar heat. Their focus is to identify thermochemical cycles that operate with solar heat and meet efficiency and cost targets as described in the following. The lower temperature option is also attractive to DOE-EERE because the solar power tower provides heat near 550°C and is near commercialization.

Based on preliminary experimental and modeling work, the Cu-Cl thermochemical cycle was chosen for further development for the following reasons:

- A maximum temperature of about 550°C was verified.
- All reactions were demonstrated at laboratory scale.
- No catalysts were needed for thermal reactions; no catalyst needed for the anode in the electrolyzer.
- The conceptual process design is based on commercially practiced technologies.
- The mass and energy balanced flowsheet showed promising efficiency.
- The H2A analysis showed potential to meet hydrogen production cost target.

Approach

The basic chemistry in the Cu-Cl cycle can be represented by the following three reactions:

This representation is simplistic and does not include any separations or phase changes and is useful for describing the cycle at a high level.

The approach has been to demonstrate the chemistry of the reactions and to optimize the operating parameters to prove the assumptions made in the modeling program. The overall focus has been to develop a process that can meet DOE's targets. The preliminary efficiency and costs are based on proving several assumptions, e.g., obtaining high yields of the desired products in the hydrolysis reaction with the minimum amount of excess water, developing a membrane that prevents copper crossover from the anode to the cathode with the electrolyzer operating at 0.7 V (2015 target) and 0.63 V (2025 target), and demonstrating that the copper oxychloride formed in the hydrolysis reactor was free flowing and decomposed over a range of temperatures. At Argonne National Laboratory, we have focused on meeting the challenges associated with the hydrolysis reaction and measured the temperature range over which the oxychloride decomposes. Partners in the INERI and NERI-C programs are focused on developing and optimizing the performance of the electrolyzer and developing methods to obtain a CuCl_2 stream suitable for the hydrolysis reactor, i.e., one that is nearly free of HCl and CuCl and contains minimal water.

The challenges in the hydrolysis reaction are the need for excess water to drive the reaction to the right

and the elimination of the parasitic reaction in which CuCl_2 decomposes to give CuCl and chlorine. In early fixed bed experiments much of the CuCl_2 remained unreacted and the amount of CuCl formed was high, in some cases greater than 20 wt%. Conditions that promoted mass transfer resulted in improved yields, about 80-90%, of the desired copper oxychloride, Cu_2OCl_2 . Smaller amounts of CuCl_2 remain unreacted and some CuCl was still observed. The results were not reproducible and a very high flow rate of a carrier gas was needed for the 80-90% yields. Therefore the primary task was to design, build and test a reactor that would provide better heat and mass transfer.

Results

In order to obtain better heat and mass transfer, we designed a spray reactor with a glass 'pneumatic' nebulizer as described in the 2008 report. Many variables, e.g. the Ar flow rates used for atomization and to deliver superheated steam, the CuCl_2 solution concentration and flowrate and the steam to copper chloride molar ratio, were optimized. While the nebulizer worked reasonably well in counter-current operation, it was difficult to use. The capillary tube in the nebulizer frequently clogged, especially in co-current operation, and the solution droplets/particles expanded in a large cone, causing deposits to form on the wall of the reactor. The nebulizer also required the use of an atomizing gas, which would not be practical commercially.

It was suggested that an ultrasonic nozzle would eliminate these difficulties [2]. After optimization of the experimental variables, very favorable results were obtained. Products consisting of $\geq 95\%$ Cu_2OCl_2 were reproducibly produced with the ultrasonic nozzle. A typical X-ray diffraction pattern is shown in Figure 1. Also shown is the standard pattern for melanothallite, the crystalline form of copper oxychloride. Comparison of the standard pattern and our product's pattern shows a one-to-one correspondence for all of the peaks except the one at d-spacing of 3.14 Å, which was assigned to CuCl. Wet chemistry analysis of the product powders showed that the CuCl was present at 3-5 wt% of the product. In addition, the product powders were very fine and free flowing. The morphology of the Cu_2OCl_2 is important because our current conceptual process design uses gravity to feed the Cu_2OCl_2 to the decomposition reactor.

The Cu_2OCl_2 powders produced with the ultrasonic nozzle were subsequently decomposed by heating them to higher temperatures. The effluent gas from the decomposition reactor was analyzed with a mass spectrometer. Figure 2 shows the evolution of oxygen as a function of temperature. The maximum temperature was 700°C. As can be seen, the oxygen signal appears from 400-550°C. Using a calibration curve, the peak

FIGURE 1. X-ray Diffraction Pattern for a Product of the Hydrolysis Reaction

area corresponded to 100% of the theoretical amount of oxygen in the starting Cu_2OCl_2 powders. No chlorine was observed in the mass spectrum.

The modeling program is focused on identifying the path forward for meeting DOE's targets for cost and efficiency. An Aspen flowsheet and a conceptual process design have been completed. The flowsheet was used to calculate the efficiency of the cycle and the conceptual process design with the H2A methodology was used to

calculate the cost of hydrogen production. The results are shown in Table 1. The conceptual process design is based on unit operations that are commercially practiced. Where a choice is available, operations are selected on the basis of low cost and high efficiency with respect to energy usage.

The results of the experimental work with the spray reactor indicated that the conceptual process design for the hydrolysis reactor was viable. A search of the literature indicated that spray reactors are in commercial operation. For example, spray reactors are used in pyrohydrolysis, a commercial process for converting MgCl_2 solutions to MgO , and in HCl recovery processes. A schematic of the hydrolysis reactor in the conceptual process design is shown in Figure 3. The feed for the hydrolysis reactor is the spent anolyte, a mixture of CuCl_2 and unreacted CuCl in an HCl aqueous solution at 24 bar and near 100°C . These parameters follow from the conditions used in the electrolysis. The electrolyzer is to be run at 24 bar (350 psi) pressure and near 100°C . The pressure is fixed at 24 bar to obtain the hydrogen gas product at DOE's target of 300 psi. A temperature near 100°C is used to minimize the cell voltage. (Proprietary work has shown that the cell voltage decreases with increasing temperature for a given current density.) The spent anolyte must be processed to remove most of the HCl and water from the

FIGURE 2. Hydrolysis Reactor in the Conceptual Process Design

TABLE 1. Results of the Calculations for Efficiency and Hydrogen Production Cost¹

Case	Capital Investment, \$M, Solar/Chemical	Cell EMF, V	Electricity Cost, \$/kW	\$/kg	Sensitivity	Efficiency, % (LHV) ²
20152	208.3/136	0.7	0.068	4.53	3.78-5.31	39
2025	168.5/106.6	0.63	0.048	3.48	2.91-4.11	41

¹The assumptions in the cost analysis are as follows:

1. Electrolyzer operates at a current density of 500 mA/cm² at above voltages.
2. Electrolysis cell area is 1.5 m² for 2015 and 3.0 m² for 2025.
3. Corrosion issues can be solved by coating with porcelain coating at a cost of 6% above carbon steel.
4. Residence times in the hydrolysis reactor are 5 sec (2015) and 2.5 sec (2025).
5. Crystallizer operates as a cooler followed by a hydroclone at 55°C.
6. Bulk HCl cost is \$241/metric ton; Bulk CuCl cost is \$7,200/metric ton
7. Cost of heliostat field can be reduced from \$127/m² in 2015 to \$90/m² in 2025.
8. Conversion factor for converting work to heat is 40%.

²Efficiency is defined as the LHV of the moles of H₂ produced divided by the sum of the heat and work. Work is converted to the thermal equivalent [1].

EMF - electromotive force

FIGURE 3. The Evolution of Oxygen from Cu₂OCl₂ as a Function of Temperature

CuCl₂. The current flowsheet specifies a crystallization process but other methods, e.g. electrodialysis, membrane distillation, and evaporative crystallization are being considered. The resulting slurry of CuCl₂ will be injected near 24 bar into the reactor. Superheated steam is injected into radial ports. The pressure of the reactor is about 0.25 bar, which is obtained by placing

an injector near the exit. As the droplets enter the hot reactor, the pressure drop should cause the slurry to form a free jet. As the CuCl₂ jet expands, it aspirates the superheated steam into the jet resulting in high mass and heat transfer between the CuCl₂ and the steam. Thus, the need for the carrier gas found to be critical in the laboratory can be eliminated in a commercial operation.

The NERI-C and the INERI members have made progress in their tasks. After the first year of these programs, it was recognized by the group that it was critical to identify a membrane material that minimizes or preferably eliminates copper crossover. Copper crossover degrades the electrolyzer's performance and prevents operation of the electrolyzer at the cell voltage and current density targets on which the current values for efficiency and cost of hydrogen production are based. Therefore, Pennsylvania State University (PSU) and AECL are both working on this task. PSU is characterizing commercial anion exchange membranes as well as developing novel chloride exchange membranes specifically designed for use in the Cu-Cl electrolyzer while AECL is examining cation exchange membranes. PSU recently reported that one of their new anion exchange membranes was stable for a relatively long period of time in conductivity tests. AECL recently reported that a new membrane material and a modified electrolyzer design resulted in a stable cell voltage for 19.5 hours in contrast to previous work in which the voltage was stable for less than 0.5 hours. Other work that is ongoing at PSU is modeling of the electrolysis reaction. The University of South Carolina (USC) is investigating electrodialysis as a means to separate Cu(II) from Cu(I) as might be found in the spent anolyte, reviewing the current Aspen flowsheet, and testing various electrolyzer designs. USC recently found that Cu(I) and Cu(II) are separable via electrodialysis. However HCl did not separate. Tulane University is developing an alternate Aspen flowsheet and conceptual process design. Its efficiency is lower than that of the current flowsheet.

Conclusions

The experimental project for the development of the hydrolysis reaction has shown that the spray reactor design provides sufficient mass and heat transfer to effectively convert all of the CuCl_2 to Cu_2OCl_2 . Tests with an ultrasonic nozzle led to improved results compared to those with a 'pneumatic' nebulizer. The modeling program has produced an Aspen flow sheet and a conceptual process design, which were used to calculate the efficiency and cost of hydrogen production. These results are based on meeting assumed values or targets for the cell voltage and current density for the electrolysis reaction and for crystallization as a method to separate CuCl and HCl from CuCl_2 in the spent anolyte.

Future Directions

- Continue experimental and modeling projects to further develop the Cu-Cl cycle.
- Continue optimization work for the hydrolysis reactor design; tests to be completed include the following: (1) determination of the minimum ratio of steam to copper for complete conversion, (2) the use of counter-current operation instead of co-current as currently used, and (3) determination of the viability of using reduced pressure to reduce the ratio of steam to copper.
- Measure the solubility of CuCl and CuCl_2 in aqueous HCl solutions as a function of temperature.

FY 2009 Publications/Presentations

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2. M.A. Lewis, J.G. Masin, and P.A. O'Hare, Evaluation of alternative thermochemical cycles-Part I The methodology. *Int. J. Hydrogen Energy* 34 (2009) 4115-4124.
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6. M.A. Lewis, Quarterly Report for the Solar Hydrogen Generation Research Program-Status of the R&D Effort for the Cu-Cl Thermochemical Cycle for Hydrogen Production, January, 2009.
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8. M.A. Lewis, Quarterly Report for the Solar Hydrogen Generation Research Program-Status of the R&D Effort for the Cu-Cl Thermochemical Cycle for Hydrogen Production, January 10, 2008.
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12. M.A. Lewis, Quarterly Report for the NHI Program-Development of the hydrolysis reactor for the Cu-Cl thermochemical cycle for hydrogen production, March, 2008.
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2. M.A. Lewis, An overview of the R&D activities for the Cu-Cl cycle, International Conference on Hydrogen Production (ICH2P), Oshawa, CA, May 3-6, 2009.
3. M.A. Lewis, An overview of R&D activities for the Cu-Cl cycle with emphasis on the hydrolysis reaction, ORF Workshop, Oshawa, CA, May 2, 2009.
4. M.A. Lewis, R&D Status for the Cu-Cl Thermochemical Cycle, Annual Merit Review, Crystal City, VA, May 18–21, 2009.
5. M.A. Lewis, R&D Status for the Cu-Cl Thermochemical Cycle, HPTT Review, Las Vegas, NV, January 22–23, 2009.
6. M.A. Lewis, Status of the R&D effort for the Cu-Cl cycle, NERI-C Consortium Technical Progress Meeting, Argonne National Laboratory, Chicago, IL, September, 2009.

7. M.A. Lewis, Status of the R&D effort for the Cu-Cl cycle, NERI-C Consortium Technical Progress Meeting, Tulane University, New Orleans, LA, April 10–11, 2008.
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II.G.2 Sulfur-Iodine Thermochemical Cycle

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Contract Number: DE-FC07-09ID14929

Project Start Date: April, 2006

Project End Date: April, 2009

Objectives

- Evaluate the potential of the sulfur-iodine (S-I) thermochemical cycle for large-scale hydrogen production using nuclear energy.
- Perform an integrated lab scale (ILS) experiment to demonstrate closed-loop operation of the S-I cycle.
- Provide the technical basis for the DOE Nuclear Energy assessment of the S-I cycle for thermochemical hydrogen production using advanced nuclear reactors.

Technical Barriers

This project addresses the following technical barriers for the Nuclear Hydrogen Initiative:

- Process chemistry and thermodynamic data information for evaluation of S-I cycle efficiency and operational characteristics.
- High-temperature, corrosion resistant materials for extended service under thermochemical process conditions.
- Thermochemical hydrogen production economics.

Technical Targets

This project is directed at the demonstration of the S-I thermochemical cycle to address large-scale hydrogen production using nuclear energy. This work

includes the investigation of the primary reaction processes, the evaluation of materials of construction, and evaluation of the cost implications of candidate design choices.

Accomplishments

Several hydrogen production experiments have been conducted this past year using the extractive distillation process developed by General Atomics. Following the initial run in April 2008, improved diagnostics and a smaller hydrogen iodide (HI) reaction vessel was incorporated to facilitate operation and control of the HI decomposition section. Multiple stand alone operations, to examine pressure dependence of H₂ production and materials behavior were conducted successfully. Parametric studies to confirm the pressure dependence of hydrogen production were conducted including a hydrogen production experiment using Commissariat à l'Énergie Atomique (CEA) Bunsen section feed material that produced approximately 75 liters/hr. All primary reactions involved in the extractive distillation process for HI decomposition (iodine extraction, HI distillation, HI decomposition, HI recycle), have now been demonstrated.

The counter-current Bunsen reactor section developed by CEA was operated several times to produce the necessary HIx (heavy) phase and H₂SO₄ (light) phase acid compositions near expected values. Significant diagnostic and hardware modifications were implemented to facilitate operations. The December 2008 run produced a HIx (heavy) phase composition that was fully consistent with flowsheet specifications. The SO₂/O₂ separation section operated reliably in multiple operations and in conjunction with the H₂SO₄ acid decomposer.

H₂SO₄ decomposition experiments were completed up to 900°C, to explore temperature, pressure, and flow rate dependencies. Multiple operations were conducted with no corrosion issues identified.

Introduction

The U.S. Department of Energy and the CEA are investigating the S-I thermochemical cycle as one of the promising methods for production of hydrogen from advanced nuclear reactors. The focus of this collaborative effort is the construction and operation of an ILS experiment that will provide the technical basis for the evaluation of this cycle. The ILS experiment will

investigate the operational characteristics, performance potential and provide input for the cost implications of this cycle to support future technology selection decisions for nuclear hydrogen production. The first thermochemical cycle to be investigated in an ILS experiment is the S-I thermochemical cycle. The ILS for S-I is being conducted as an International Nuclear Energy initiative (INERI) project and is a collaborative effort involving Sandia National Laboratories (SNL), General Atomics (GA), and the CEA. The CEA is designing and testing Section 1, the primary (Bunsen) reaction section. GA is developing and testing Section 3, the HI decomposition section. SNL is developing and testing Section 2, the high temperature H_2SO_4 decomposition section.

Approach

- Flowsheet analysis of the SI-cycle process to evaluate alternative configurations.
- Experiments to investigate the chemistry of the three major reactions for the S-I cycle.
- Develop improved materials and heat exchanger designs for service in high temperature corrosive environments.
- Design and construct an ILS apparatus to provide a test bed for S-I cycle evaluation.
- Perform ILS experiments to evaluate closed-loop operation.
- Develop system designs, sizing, and materials for a nominal megaWatt pilot-scale experiment.

Results

During the past year, the focus has been on characterizing the individual process sections and on coupling the operation of the three sections in a closed loop. All three sections have been operated successfully multiple times and partially integrated operations have been conducted.

Bunsen Reaction

The final Bunsen reaction experiments focused on demonstrating repeatable successful, controlled operation of the Bunsen reactor and its associated components. Prior to the final experimental run, a team of engineers and technicians from CEA were on site to make several modifications to the Skid 1 hardware to enhance the reliability of the system. The primary modifications dealt with the HIX (lower phase) product flow control. These modifications allowed for a successful Bunsen reactor during March of 2009. The operations demonstrated the successful control of both the upper and lower phase product flows, reactor pressure and temperature control as well as the reactant

flow control (water, sulfur-dioxide and iodine). Samples of the process fluids from the experiment have been analyzed. The upper phase material was dilute, at 12 wt% H_2SO_4 , while the lower phase was close to target at 40 wt% HI. The concluding experiments for phase 3 testing of the S-I ILS process have been completed.

Sulfuric Acid Decomposition

The SNL acid decomposition process has been operated several times in stand-alone mode and while integrated with the CEA process section. Stand-alone tests verified process operation after completion of process modifications. The integrated tests with the CEA section involved production of sulfur dioxide and subsequent transfer to the CEA skid. Parametric operations evaluated the effect of decomposition temperature on acid decomposition efficiency. All tests were performed at a pressure of 2 bar absolute with 41 mole percent acid feed. The results from varying the decomposition temperature from 650 to 850°C are given in Table 1.

TABLE 1. Results for Temperature Effect on Decomposition Efficiency

Acid decomposition temperature (°C)	O_2/SO_2 ratio	Gas ($\text{SO}_2 + \text{O}_2$) flow rate (L/hr)
850	0.48	2.4 ± 0.1
800	0.5	2.2 ± 0.1
750	0.47	1.8 ± 0.1
700	0.56	1.1 ± 0.2
650	No SO_2 detected	0

The results match analytical estimates of sulfur dioxide production as a function of temperature. No gas was produced at 650°C. The data indicate for maximum

FIGURE 1. SO_2 Production versus Acid Flow Rate (40 m/o, 850°C)

FIGURE 2. Production of SO_2/O_2 as a Function of Decomposition Temperature

conversion under the conditions of the test the acid decomposer must be operated at 800°C or higher. These data are shown in Figures 1 and 2.

HI Decomposition

The primary variable investigated during this period is the operating pressure which determines the HI recycle rate and therefore the effective hydrogen production rate. Several runs have been conducted at pressures ranging from 45-200 psig. The primary affects of the pressure are 1) the hydrogen production rate and 2) the HI distillation boiler temperature. The system pressure affects H_2 production rate by affecting the HI recycle. As the decomposition step is only 20% efficient, the un-reacted HI needs to be recycled in order to achieve the target production rates. This recycle is achieved by cooling the HI/ H_2 stream to ~5°C after the iodine has been removed. The vapor pressure of HI at this temperature is 66.15 psia. As the system pressures exceed this value, the percentage of HI liquefied increases as the vapor fraction of HI decreases by Henry's Law:

$$Y_{\text{HI}} = P_{\text{HI}}/P_{\text{tot}}$$

As the total pressure increases, a larger fraction of HI is condensed to liquid, and recycled back to the reactor. The hydrogen production as function of pressure is shown in Figure 3.

ILS Status

These experiments conclude the phase 3 testing of the ILS. While the final tests focused on the successful operation of the Bunsen reactor, previous experiments had confirmed the integrated operation capabilities of the entire loop.

FIGURE 3. H_2 Production Rate as a Function of Pressure

Conclusions and Future Directions

The DOE-CEA project on the ILS was completed in April 2009. The ILS equipment is being cleaned and put in safe shutdown condition, and the system will be decommissioned in Fiscal Year 2010. The results from the project included several partially integrated runs conducted to produce H_2 at up to 75 l/hr. Bunsen operations produced correct lower phase compositions, but Iodine flow challenges limited reliability. The HI section operations show extractive distillation works well, but it is complex and considered to be too costly for large-scale applications. Initial experiments on reactive distillation show promise as a more efficient and lower cost alternative distillation path. The SNL SiC bayonet acid decomposer has operated routinely with no materials issues. Among the observations from these experiments is the difficulty in finding affordable and reliable components at small scales. A larger scale experiment would allow wider component and materials options. Materials issues encountered in the HI section study identified critical areas for future development.

FY 2009 Publications

1. Moore, R.C., E. Parma, Russ, B., Sweet, W., Helie, M., Pons, N., and P. Pickard. (2008) "An Integrated Laboratory-Scale Experiment on the Sulfur-Iodine Thermochemical Cycle for Hydrogen Production", 4th International Meeting on High Temperature Reactor Technology, Washington, D.C., September 2008.

FY 2009 Presentations

1. April 2008, NHA Meeting (Sacramento) "Status of the INERI Sulfur-Iodine Integrated Loop Experiment".
2. October 13–18, 2008, Pacific Basin Nuclear Conference (Aomori, Japan), "S-I Integrated Lab Scale Demonstration Update".

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4. 18 June, 2008, World Hydrogen Energy Conference, (Brisbane, Queensland). “Demonstrating Production of Hydrogen using the Sulfur-Iodine Hydrogen Cycle”
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II.G.3 Hybrid Sulfur Thermochemical Cycle

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Project Start Date: June 1, 2004

Project End Date: September 30, 2009

Technical Targets

DOE's Office of Nuclear Energy has the lead responsibility for hydrogen production utilizing nuclear energy for high-temperature (700°-1,000°C) thermochemical water-splitting chemical cycles. The Office of Hydrogen, Fuel Cells and Infrastructure Technologies will collaborate with Nuclear Energy (NE) on the thermochemical hydrogen production research and development activities. This project addresses the goal of the Nuclear Hydrogen Initiative (NHI) [1] to demonstrate the economic, commercial-scale production of hydrogen using nuclear energy.

The project is conducting component development and unit testing for an SDE, which is the key component of the HyS thermochemical process. Insights gained from this work will be applied toward the design, scale up and demonstration testing of a complete HyS process meeting the NHI goals for interfacing with advanced nuclear reactors.

Accomplishments

- Established collaborations with leading proton exchange membrane (PEM) suppliers and characterized the ionic conductivity, SO₂ diffusion and chemical stability of over 15 advanced membranes.
- Organized and hosted an international workshop on SDE technology.
- Completed testing of 11 additional (37 total) single-cell electrolyzer configurations at temperature of 80°C and pressure to 700 kPa.
- Upgraded test facility to permit unattended 24/7 operation.
- Invented a new operating method to prevent sulfur build-up inside of the cell.
- Completed two 200+ hour tests of electrolyzer demonstrating operation without sulfur build-up limitations.
- Completed major conceptual design and cost study of HyS process demonstrating potential for >40% thermal efficiency and competitive cost of hydrogen when coupled with an advanced Generation IV gas-cooled nuclear reactor.

Introduction

High temperature (750-900°C) thermal energy can be utilized in thermochemical water-splitting cycles to produce hydrogen with no greenhouse gas emissions.

Objectives

- Develop the Hybrid Sulfur (HyS) thermochemical water-splitting process for hydrogen production using heat from advanced nuclear reactors.
- Optimize the cycle design and establish design requirements for key components.
- Design and demonstrate an SO₂-depolarized electrolyzer (SDE) capable of operating at low voltage (<600 mV) and high current density (>500 mA/cm²).
- Characterize, analyze and select cell components, including proton exchange membrane.
- Conduct electrolyzer tests demonstrating successful operation without sulfur limitations.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

(H) System Efficiency

(U) High-Temperature Thermochemical Technology

(V) High-Temperature Robust Materials

The HyS Process uses two linked chemical reactions to produce hydrogen in an electrochemical reaction and oxygen in a thermochemical reaction [2]. Sulfur dioxide is used to depolarize the anode in a water electrolyzer, creating sulfuric acid and releasing the hydrogen. Heat is used to thermally decompose the acid, regenerating the sulfur dioxide and releasing the oxygen. Central solar receivers or high temperature gas-cooled nuclear reactors can be used to supply the heat. The process has the potential for high efficiency, competitive cost of hydrogen, and it has been demonstrated at a laboratory scale to confirm performance characteristics. A simplified block schematic showing the major process steps is shown in Figure 1.

A major challenge for the HyS cycle is the development of an efficient, cost-effective electrochemical reactor, or SDE. The use of SO_2 -depolarization reduces the standard cell potential from 1.23 V for conventional water electrolysis to 0.158 V, dramatically reducing the electricity required per unit of hydrogen production. This project focuses on the development of the SDE. The SDE must be capable of operation at low voltage (<600 mV), high current density (>500 mA/cm²), long-life ($>40,000$ hours) and competitive capital cost. A companion project under the DOE-NE NHI [3] involves the development of the high temperature acid decomposition system, which is required to close the cycle. Upon establishment of these two technologies, an integrated lab-scale experiment will be conducted to demonstrate closed-loop operation. If successful, the process will be scaled up for demonstration with DOE's Next Generation Nuclear Plant (NGNP), which is scheduled to be built at the Idaho National Laboratory by year 2021 [4].

Approach

In contrast to past efforts by others to develop an SDE, Savannah River National Laboratory (SRNL) has based its work on the use of PEM technology. The advantages of this design concept include high electrochemical efficiency, small footprint, and potential for competitive capital cost, all of which are crucial

HTGR - high-temperature gas-cooled reactor

FIGURE 1. Simplified Block Schematic of Hybrid Sulfur Thermochemical Cycle

for successful implementation on a commercial scale. Since PEM technology is also the subject of intense development efforts for use in automotive fuel cells and direct methanol fuel cells, there is the opportunity for leveraging that work for improving the SDE. The application is challenging, however, since the SDE must react sulfur dioxide with water to produce hydrogen in the presence of strong sulfuric acid under elevated temperature and pressure.

To achieve the project objectives, a component development project to identify, characterize and select the best PEM electrolyte, electrocatalysts, and associated cell components is being conducted. Button cell testing is used to verify promising alternatives. Advanced membranes that have lower water content and can operate at higher temperature (120 to 140°C) appear the most promising. Single cell electrolyzers of approximately 60 cm² active cell area are then used to conduct proof-of-concept tests and determine performance and lifetime. Post-test examinations using scanning electron microscopy (SEM) are used to examine the PEMs to determine if sulfur deposits have accumulated inside. Avoidance of sulfur build-up is a key requirement for long-term cell operation. Successful configurations will then be assembled into multi-cell stacks, as well as being scaled up to larger cell sizes. The SDE can then be combined with an acid decomposition system and balance of system components to demonstrate integrated HyS Process operation.

Results

In the past year, the main focus has been on the exploration of high temperature membranes and SDE operation without sulfur limitations. Collaborations were established with leading researchers and membrane developers from industry, academia and national laboratories. During the selection process of commercially available and experimental membranes, an array of thicknesses, equivalent weights, chemistry, and reinforcements were considered. Commercial membranes include perfluorinated sulfonic acid (PFSA) membranes, such as DuPont Nafion[®], which was chosen as the benchmark for comparing membrane performance. Many of the experimental membranes were prepared exclusively to reduce the transport of inert species, such as dissolved SO_2 . A number of these membranes were already under development for use in direct methanol fuel cells, which have a similar crossover problem involving methanol. SRNL hosted an information exchange and workshop in 2009 to discuss SDE membranes and related research areas. It was attended by many of the leading PEM experts in the country, as well as representatives from five countries. The presentations and workshop results can be assessed on the SRNL Web site [5]. A list of the some of the

membranes selected and characterized by SRNL in the past year is given in Table 1.

TABLE 1. Membranes Selected and Characterized by SRNL

Membrane Type	Supplier
Perfluorinated sulfonic acid (PFSA)	DuPont
Polybenzimidazole (PBI)	BASF (Germany)
Sulfonated Diels-Alder polyphenylenes (SDAPP)	Sandia National Laboratories
Stretched recast PFSA	Case Western Reserve University
Nafion®/fluorinated ethylene propylene (FEP) blends	Case Western Reserve University
Treated PFSA	Giner Electrochemical Systems LLC
Perfluorocyclobutane-biphenyl vinyl ether (BPVE)	Clemson University
Perfluorocyclobutane-biphenyl vinyl ether hexafluoroisopropylidene (BPVE-6F)	Clemson University

An ideal membrane has high proton conductivity and low SO_2 transport. These parameters were evaluated using a custom-made permeation cell; a schematic of the cell is shown in Figure 2. The cell consists of two glass chambers joined by a Teflon® bridge where the membrane is secured. During measurements both chambers were filled with the concentrated acid of interest (typically 30 wt% H_2SO_4) and purged of oxygen by flowing nitrogen. A constant potential is applied and the SO_2 transport through the membrane is determined by measurement of the current as a function of time. The test unit was also modified to perform as a small electrolyzer in order to compare the performance of various membranes and electrocatalysts. Membrane

FIGURE 2. Simplified Schematic of the SO_2 Transport Characterization Cell

electrode assemblies (MEAs) were fabricated and installed in the apparatus, which was then operated as a button-cell electrolyzer. A two electrode system was used with a potential of 1.1 V applied across the cell. Testing was limited to atmospheric pressure, and typically operated at 60-80°C. Each membrane was also tested for through-plane ionic conductivity using electrochemical impedance spectroscopy. The results are shown in Figure 3.

The lowest SO_2 transport coefficient was measured for membranes of the DuPont bilayer and high equivalent weight PFSA, but these also showed unacceptably low ionic conductivity. The best combined performance (low SO_2 transport and high conductivity) was observed for PBI, BPVE, and Case Nafion®-FEP blend. These test results were determined at 67°C and atmospheric pressure. Several of the more promising membranes, such as the Clemson BPVE and Sandia SDAPP, are expected to perform better at higher temperature (120-140°C). This requires pressurization in order to maintain an adequate concentration of SO_2 in the anolyte. A new pressurized button cell test facility is being constructed to permit testing at up to 150°C and 2 MPa in order to fully explore the higher temperature membranes. Giner Electrochemical Systems LLC is supporting SRNL in this work, including construction of a major portion of the pressurized button-cell test facility and construction of multi-cell SDE stacks. This helps to leverage Giner's experience in manufacturing commercial PEM water electrolyzers.

A major goal of the past year's HyS research project was to demonstrate operation of an SDE without sulfur layer build-up inside of the MEA. PEM electrolytes require hydration for efficient operation, which can permit neutral species, such as sulfur dioxide, to pass through the membrane. In the SDE, sulfur dioxide that diffuses through the membrane from the anode to the cathode can be reduced to elemental sulfur, which is an

FIGURE 3. SO_2 Diffusion and Conductivity Results for SDE Membranes

unwanted side reaction. Most of the prior SDE tests at SRNL resulted in sulfur build-up inside of the cell's MEA, a phenomenon that reduces performance and limits operating lifetime. Figure 4 is an SEM micrograph showing the result of sulfur layer formation.

In response to this technology challenge, SRNL devised a new operating method (patent applied for) that significantly reduces the amount of sulfur dioxide available to diffuse through the membrane. The small amount of SO_2 that does reach the cathode is converted into hydrogen sulfide gas, rather than elemental sulfur, and it exits the cell along with the hydrogen, thus avoiding the life-limiting build-up of sulfur inside of the MEA. This is a major breakthrough in permitting PEM cells to be used in the SDE mode. The new sulfur-limiting operating method was successfully demonstrated in a series of single cell electrolyzer tests, using a Nafion® membrane with a 54 cm^2 active cell area. A 50-hour and two 212-hour longevity tests were conducted. Physical observations during testing indicated a noticeable reduction in sulfur presence, and post-test visual examinations of the SDE indicated good cell integrity and no appearance of sulfur on the MEA. The final test run was conducted continuously for 212 hours prior to a controlled shutdown. The cell voltage was extremely stable throughout, as shown in Figure 5. Operating conditions included a cell temperature and pressure of 80°C and 172 kPa, respectively. The current density was maintained at 500 mA per cm^2 , which is the commercial design goal. Measurement of hydrogen production closely matched the theoretical value, indicating very good current efficiency. The cell voltage was approximately 760 mV, which is above the commercial goal of 600 mV. However, operation

Sulfur formation is evident after multiple hours of SDE operation

FIGURE 4. SEM Micrographs Depicting Sulfur Formation Inside MEA

FIGURE 5. Voltage vs. Time for MEA No. 37

at higher temperature and pressure and the use of advanced membranes are expected to reduce the voltage in future configurations.

The MEAs from each of the tests were examined by various analytical methods to verify the absence of sulfur build-up. SEM and energy dispersive X-ray analysis were used to examine multiple locations on each layer of the MEAs. Results showed no localized concentration of sulfur and no evidence of a precursor stage to a sulfur-rich build-up layer. These results confirm that operation of the SDE using the sulfur-limiting method successfully prevents sulfur accumulation inside of the cell.

In addition to the experimental work on the SDE, a comprehensive conceptual design and cost study was performed in conjunction with industry partners for an integrated nuclear hydrogen plant employing the HyS Process and a Generation IV advanced nuclear reactor. The HyS flowsheet was optimized, and the overall plant configuration was modified to permit substantially more hydrogen production per nuclear reactor than the previous concept. The overall thermal efficiency and cost of hydrogen from the nuclear hydrogen plant were deemed attractive as a future greenhouse gas-free hydrogen production option, especially for delivering hydrogen to large industrial users, such as chemical, oil refining and synthetic fuel plants.

Conclusions and Future Directions

The HyS Process is one of the most promising candidates for thermochemical hydrogen production using heat for advanced nuclear reactors or solar central receivers.

- In 2009, a major breakthrough in SDE development was achieved by demonstrating a method of operation that permits the use of PEMs without the limitation of sulfur layer build-up inside of the MEA.

- Collaborations were established with leading PEM developers; several promising high temperature membranes were identified, indicating high probability of meeting the commercial performance goals previously established for the SDE.
- Design and cost studies performed in collaboration with industry indicate that an integrated advanced nuclear reactor and HyS hydrogen plant could be an attractive greenhouse gas-free hydrogen production option.

The DOE-NE NHI will be concluded at the end of Fiscal Year 2009, with responsibility for hydrogen process development assumed by the NGNP program. If HyS is selected, the next activities may include testing of high temperature membranes, scale up to larger SDE cell sizes, construction of a multi-cell stack, and demonstration of an integrated lab-scale experiment of a complete HyS Process, including the SDE and acid decomposition steps.

Special Recognitions & Awards/Patents Issued

1. Program met a DOE-NE Level 1 Milestone by demonstrating SDE operation without sulfur build-up limitations using an innovative operating method. A patent has been applied for.

FY 2009 Publications/Presentations

1. W.A. Summers, "Hybrid Sulfur Thermochemical Cycle," 2009 DOE Hydrogen Program Review, Presentation PD#13, Arlington, VA, May, 2009.
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3. W.A. Summers, "Development Status of the Hybrid Sulfur Thermochemical Production Process," OECD/NEA Fourth Information Exchange Meeting on Nuclear Production of Hydrogen, Oakbrook, IL, April 14, 2009.
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8. M. Gorenssek et al., "Hybrid Sulfur Process Reference Design and Cost Analysis," DOE Information, www.osti.gov/bridge/ ID: 956960 (2009).
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2. W. Summers, M. Gorenssek, M. Buckner and Z. Qureshi, "Conceptual Design for a Hybrid Sulfur Thermochemical Hydrogen Production Process," *ANS Transactions*, **92**, 101 (2005).
3. P. Pickard, "Sulfur-Iodine Thermochemical Cycle," DOE Hydrogen Program, 2008 Annual Progress Report, November, 2008, pg. 226-228.
4. Department of Energy's Next Generation Nuclear Plant, <http://www.nextgenerationnuclearplant.com/>.
5. "Hybrid Sulfur Electrolyzer Workshop and Information Exchange", Savannah River National Laboratory, Aiken, SC, April 20-21, 2009, http://srnl.doe.gov/hse_workshop/index.htm.

II.G.4 Laboratory-Scale High Temperature Electrolysis System

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Start Date: January 23, 2003

Projected End Date: Engineering Demo, 1 MW,
2018

- Develop energy-efficient, high-temperature, solid-oxide electrolysis cells (SOECs) for hydrogen production from steam.
- Develop and test integrated SOEC stacks operating in the electrolysis mode.
- Develop optimized plant configuration for coupling to Generation IV Reactor.
- Combine components in an Integrated Laboratory-Scale (ILS) experiment.
- Scale up to a 200 kW pilot plant and a 1 MW engineering demonstration facility.

** Since there are no objectives specific to the nuclear production of hydrogen, we have adopted those cited from wind water electrolysis.*

Technical Barriers

This project addresses the following technical barriers of the Multi-Year Program Plan p. 3.1-24 and the Nuclear Hydrogen Initiative:

- **G. Capital Cost** – Development of larger systems is also needed to take advantage of economies of scale.
- **H. System Efficiency** – New membrane, electrode and system designs are needed to improve system efficiency.
- **I. Grid Electricity Emissions** – Low-cost, carbon-free electricity generation is needed. Electrolysis systems that can produce both hydrogen and electricity need to be evaluated.

Technical Targets

- No greenhouse gas releases from industrial scale H₂ production.
- Energy efficiency: 50% (lower heating value of H₂ produced/total thermal output of reactor).
- Cost of hydrogen: \$3.10/kg – centralized production only, 2012.
- Life of cells: 20,000 hours of continuous operation.

Contribution to Achievement of DOE Systems Analysis Milestones

This project contributed/will contribute to achievement of the following DOE systems analysis milestones from the Systems Analysis section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

Objectives

- By 2012, reduce the cost of central production of hydrogen from high temperature electrolysis to \$3.10/gasoline gallon equivalent (gge) at plant gate, by 2017, reduce the cost of central production of hydrogen from high temperature electrolysis to <\$2.00/gge at plant gate.*

- **Milestone 2:** Complete baseline economic, energy efficiency and environmental targets for fossil, nuclear and renewable hydrogen production and delivery technologies. (4Q, 2005)
- **Milestone 8:** Complete analysis and studies of resource/feedstock, production/delivery and existing infrastructure for technology readiness. (4Q, 2014)
- **Milestone 10:** Complete an analysis of the hydrogen infrastructure and technical target progress for technology readiness. (2Q, 2015)
- **Milestone 11:** Complete environmental analysis of the technology environmental impacts for the hydrogen scenarios and technology readiness. (2Q, 2015)

Accomplishments (Fiscal Year 2009)

- Demonstrated improved performance of oxygen and steam hydrogen electrodes through the deposition of electrocatalytic materials by atomic layer deposition or other infiltration processes. (Argonne National Laboratory) 9/30/2008
- Completed analysis of hot oxygen handling and cooling options based on collaboration with Atomic Energy Canada, Limited. 7/2/2008
- Tested the three-module (each module 4 x 60 cells) for the ILS experiment for 1,080 hours in Idaho Falls with a maximum output of 5.65 N m³ H₂/hour (0.504 kg H₂/hour). 9/5/2008-10/20/2008
- Completed analysis report on corrosion testing of the second series of balance of plant materials on 9/30/2008.
- Completed report on experimental data from the operation of the High Temperature Electrolysis (HTE) ILS experiment on 2/17/2009.
- Completed report on critical causes of stack degradation in ILS cells on 5/27/2009.
- Demonstrated low-degradation performance of a 10-cell stack using improved oxygen electrodes, 5/27/2009-9/8/2009.

Introduction

A research program is under way at the Idaho National Laboratory and collaborating laboratories to assess the performance of solid oxide cells operating in the steam electrolysis mode for hydrogen production over a temperature range of 800 to 900°C. The research program includes both experimental and modeling activities. The electrolysis cells are electrolyte-supported, with scandia-stabilized zirconia electrolytes (~140 µm thick), nickel-cermet steam/hydrogen

electrodes, and manganite oxygen electrodes. The metallic interconnect plates are fabricated from ferritic stainless steel. In the last year we have begun testing various electrode-supported configurations as well.

During FY 2009, experimental results were obtained from three modules of four 60-cell stacks each, fabricated by Ceramtec, Inc. Additional experiments at ANL, MIT, and INL investigated the characteristics of cells used in previous tests and the performance of a variety of materials being considered for use in the balance of plant for HTE hydrogen production plants. We also organized a workshop on the long-term degradation of solid oxide cells used in high temperature electrolysis in conjunction with the Fuel Cell Seminar in Phoenix, October 27, 2008.

Approach

High-temperature electrolysis testing of single button cells and stacks has been in progress at the INL and the subcontractor Ceramtec Inc. (Salt Lake City, UT) since 2003. The scales of testing accomplished to date at the INL are pictured in Figure 1. The ILS facility operated at a maximum hydrogen production rate of 5,650 normal (273°K, 1 atm) L/hr (0.504 kg H₂/hr) with an input of 18 kWe. The ILS operated continuously for 1,080 hours from September 5 through October 20, 2008. Because of degradation of the oxygen electrodes, the hydrogen output decreased to 800 NL/hr in the course of the test.

After each of the tests, the stacks have been disassembled and the cells have been destructively examined to determine elemental migration during the test and to detect changes in the morphology of the electrolyte and electrodes. These examinations have also been conducted on cells in the test of the three-module ILS.

FIGURE 1. General View of the HTE ILS Experiment

Results

The full, three-module ILS experiment operated in Bay 9 of the Bonneville County Technology Center, Idaho Falls, from September 5 through October 20, 2008, a total of 1,080 hours [1]. A 420-hour test of the ILS with a single module was conducted in September and October 2007 [2]. The general layout of the experiment is shown in Figure 1, with the numbered components listed in Table 1.

TABLE 1. Identifiers for Figure 1

ID	Component
1	Hot zone enclosure lid
2	Power supply and instrument racks
3	Electrical distribution cabinet
4	Data acquisition and control monitors
5	Deionized water system
6	Steam generator
7	Steam and H ₂ superheaters
8	Air compressor
9	Patch panel
10	Product finned cooler
11	Steam condenser
12	Mass flow controllers
13	H ₂ vent
14	Air and O ₂ vent

As can be seen in Figure 1, the ILS contains most of the components needed in a full-scale high temperature electrolysis plant, with exception of the nuclear reactor and facilities for using the hydrogen produced. The three modules, with the associated voltage taps and thermocouples are shown in Figure 2a, immediately before the closure of the hot zone lid.

Two capabilities were added to ILS between the single module and the three-module tests. In order to more closely simulate the operation of a commercial hydrogen plant, we added a system for recycle of 10-30% of the product hydrogen back into the input steam to maintain reducing conditions on the steam/hydrogen electrodes of the cells within the modules. Secondly, we installed heat recuperators under the modules to allow the use of steam at 350° to 450°C, rather than the 800°C required at the input to the modules. As shown in Figure 2b, the heat in the hydrogen and oxygen product streams at ~820°C is used to heat the input streams to ~790°C. The inherent ohmic heating in the cells provides the required 20°-40°C temperature difference between the countercurrent streams.

Heat up of the INL three-module ILS system began at approximately 5 PM on September 4, 2008. Peak

FIGURE 2. (a) Three modules each containing four stacks of 60 cells. The six recuperators are partially covered in insulation below the modules. (b) A screen print from our LabView® control software, showing the temperatures of the various streams entering and leaving the two recuperators under module 1.

hydrogen production as well as peak electrolysis power input was achieved at approximately 10 AM on September 5, 2008 (~17 hours elapsed test time). At this time, the electrolysis modules were consuming 18 kW of electrical power and producing over 5.7 Nm³/hr H₂. Early test module area-specific resistance (ASR) values ranged from 1.25 Ω-cm² to just over 2 Ω-cm². Testing continued for 1,080 hours. Significant module performance degradation

was observed over the first 480 hours, after which no further degradation was noted for the remainder of the test for modules 1 and 2, while module 3 continued to degrade. The total H_2 production rate decreased from $5.7 \text{ Nm}^3/\text{hr}$ to a steady-state value of $0.7 \text{ Nm}^3/\text{hr}$, primarily due to cell degradation. Most of the test was conducted at a constant electrolyzer power supply voltage of 76 V.

Once all test objectives had been successfully met, the test was terminated in a controlled fashion. Two relatively minor problems were encountered during testing. First, one N_2 mass flow controller failed and was replaced with a rotameter without any disruption of the experiment. Second, water condensation occurred in the H_2 recycle system. This was due to the elevated pressure required in the H_2 recycle loop. The condensate would sometimes collect in and interfere with the inlet H_2 mass flow controllers, leading to periodic interruptions in the hydrogen recycle flow. This may have caused accelerated degradation of the ILS modules. In particular, the flow interruptions could have caused electrode oxidation to occur in the modules. Once H_2 flow resumed, reduction would occur on the electrode surfaces. This cycling of oxidation and reduction may have contributed to the high rate of performance degradation observed. Around 480 hours elapsed test time, the condensate problem was finally fixed by installing a water trap just upstream of the H_2 mass flow controllers. Subsequent to this, the ASR values for modules 1 and 2 improved and finally leveled out with no further degradation. The reason for the continued performance degradation of module 3 after the condensation problem was solved while modules 1 and 2 improved is not understood.

The effectiveness of the heat recuperation system was estimated. A comparison was made between heater loads, steam generator loads, and hot zone heat losses between the earlier single module test (no heat recuperation) and the present three module test (with heat recuperation). The total per-module electric heater power was reduced by 50% in the case of heat recuperation.

Once the condensation problem was solved, the hydrogen recycle system worked flawlessly and made unnecessary the use of any external hydrogen source for maintaining reducing conditions in the cells.

The facility instrumentation and data acquisition/control system performed as designed except for condensation interfering with the inlet hydrogen mass flow controllers and failure of one nitrogen mass flow controller. Both problems were circumvented/solved without any disruption of the experiment.

Overall, the facility successfully demonstrated the largest scale high temperature solid oxide-based production of hydrogen to date.

Post-test examination of the representative cells from the three-module ILS test indicated that the oxygen electrode had delaminated from the electrolyte over part of the electrolyte area [3]. After a series of short-term tests of various diffusion-barrier layers in the cells, a long-duration test of a 10-cell stack was started May 27. As of this writing, that stack has operated ~1,000 hours and has shown only about 5% degradation. It is expected that this test will run until the end of FY 2009.

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II.H.1 Photoelectrochemical Hydrogen Production: DOE PEC Working Group Overview

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Contract Number: Various funded projects within the DOE PEC Working Group with different contract numbers.

Project Start Date: Initiation of U.S. DOE PEC Working Group, 2004: Various funded projects within the DOE PEC Working Group with different start dates.

Project End Date: Various funded projects within the DOE PEC Working Group with different end dates within 2009/2010.

- (AC) Device Configuration Designs
- (AD) Systems Design and Evaluation
- (AE) Diurnal Operation Limitations

Technical Targets

As recognized within the PEC Hydrogen research community and the DOE PEC Hydrogen program, the technology is still far from maturity, and the most critical technical issues relate to the development of suitable photoactive semiconductors for water-splitting. This is reflected in Table 1, a reprint of the DOE Targets for PEC Hydrogen Production from the DOE's Multi-Year RD&D Plan [1].

TABLE 1. DOE Targets for Photoelectrochemical Hydrogen Production

Characteristics	Units	2003 Status	2006 Status	2013 Target	2018 Target
Usable semiconductor bandgap	eV	2.8	2.8	2.3	2.0
Chemical conversion process efficiency	%	4	4	10	12
Plant solar-to-hydrogen efficiency	%	not available	not available	8	10
Plant durability	hr	not available	not available	1,000	5,000

Objectives

The U.S. DOE's photoelectrochemical (PEC) Hydrogen Production Working Group's primary objective is to collaboratively develop practical solar hydrogen-production technology, using innovative semiconductor materials and devices research and development (R&D) to foster the needed scientific breakthroughs for meeting DOE Hydrogen Program goals.

Technical Barriers

The DOE PEC Working Group is working to address all of the technical barriers identified in the "Photoelectrochemical Hydrogen Production" section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (Y) Materials Efficiency
- (Z) Materials Durability
- (AA) PEC Device and System Auxiliary Material
- (AB) Bulk Materials Synthesis

The DOE PEC Working Group is utilizing its collective expertise in theoretical materials modeling, synthesis, characterization and analysis to study a diverse portfolio of promising PEC thin-film materials classes with the potential for meeting the technical targets.

Accomplishments

Important milestones have been achieved this past year through the collaborative efforts of the DOE PEC Working Group, and the associated DOE-funded projects. Significant progress has been made in the development of the Working Group's "Tool Chest" of materials theory, synthesis, characterization and analysis techniques; and this tool chest has been instrumental in the development and optimization of important PEC materials classes. For example, "useable band gaps" of 2.6 eV have been demonstrated in tungsten-based films compatible with integration into multi-junction devices with 5% chemical conversion efficiency, and even lower band gaps have been demonstrated in other PEC materials classes, including iron-oxide, silicon-carbide,

copper-chalcopyrites, molybdenum-sulfide, and III-V compounds. DOE PEC Working Group efforts are ongoing to render these band gaps “useable” for high-efficiency PEC hydrogen production. The PEC Working Group accomplishments, detailed further in following sections, can be summarized broadly as follows:

- Successful Development and Application of New PEC “Tool-Chest” Capabilities.
- Advances in Focus Materials Classes Using the DOE-PEC Working Group’s “Tool-Chest.”
- Further Expansion of Collaborative Research Efforts.

Introduction

PEC hydrogen production, the splitting of water into hydrogen and oxygen using sunlight, is an important enabling technology for a future green economy which will rely, in part, on hydrogen as an energy currency [2]. The traditional semiconductor-based PEC material systems studied to date, however, have been unable to meet all the performance, durability and cost requirements for practical hydrogen production. For example, PEC semiconductors such as titanium-dioxide and other metal-oxides have proven to be stable in aqueous solutions, but suffer from low solar conversion performance due to their high band gaps [3]. Based on these inherent limitations, it has become increasingly clear that new, more advanced materials need to be developed. Technology enabling breakthroughs in materials R&D are needed for the success of PEC hydrogen production.

Toward this end, the U.S. DOE currently funds a number of research institutions from the academic, industrial and national laboratory sectors with the objective of discovering, engineering and optimizing such advanced PEC materials systems for solar water-splitting. To facilitate progress, the project participants, have formed a national Working Group on PEC hydrogen production, bringing together experts in analysis, theory, synthesis and characterization from the academic, industry and national laboratory research sectors. The 2009 DOE Hydrogen Program Annual Merit Review (AMR) held in Crystal City, VA featured 13 presentations from participating PEC Working Group institutions, as illustrated in Figure 1. An overview of the collective approach and past-year’s progress is presented in the following sections.

Approach

The general approach of the collaborative effort among the DOE PEC Working Group researchers is to integrate state-of-the-art theoretical, synthesis

FIGURE 1. PEC Working Group Members with current DOE financial support, including the 2009 DOE Hydrogen Program Annual Merit Review oral/poster presentation designations.

and analytical techniques to identify and develop the most promising materials classes to meet the PEC challenges in efficiency, stability and cost. From the application of density-functional theory to calculate band-structures and effects of co-incorporants on valence and conduction band positions; through the use of diverse synthesis techniques, including combinatorial methods, to create tailored materials; and by employment of microstructural, electron spectroscopic, and electrochemical characterization techniques, a comprehensive picture of the materials properties and resulting performance is being developed. Within the DOE PEC Working Group, the approach has been applied to a number of “focus materials” deemed of particular interest for PEC applications.

It is important to stress that PEC hydrogen production has already been successfully demonstrated on the laboratory scale. High solar-to-hydrogen (STH) efficiencies, between 12-16%, have been demonstrated for limited durations in devices based on expensive high-quality crystalline semiconductors, such as the III-V tandem GaAs/GaInP₂ cell [4]. In addition, lower STH efficiencies, in the 3-5% range have been demonstrated in devices based on lower priced thin-film semiconductor materials. Multi-junction devices, for example using WO₃ films as a PEC top-junction, have been reported in this performance category [5]. To achieve practical PEC hydrogen production, new semiconductor materials systems with both high performance and low cost are needed. One specific approach is the further development of the traditional PEC semiconductor thin-films and nano-structures for higher efficiencies. Examples include improvements to iron-oxide and tungsten trioxide. Another approach is the adaptation of efficient photovoltaic (PV) semiconductor thin-films and nano-structures for effective use in PEC. This includes, for example, copper chalcopyrites and amorphous silicon compounds. Other innovative approaches include the development

of entirely new materials classes, such as quantum-confined WS_2 and MoS_2 nanoparticle systems; and the development of breakthrough synthesis technologies to reduce the cost of high-performance crystalline semiconductors, such as $\text{GaAs}/\text{GaInP}_2$. Future progress in all these approaches will be integrally tied to the DOE PEC Working Group's continued development and deployment of its tool-chest, and continual feedback among the theory, synthesis and characterization efforts

Results

To expedite technical progress, the DOE PEC Working Group has initiated task forces to coordinate important PEC research activities. While some of the collaborative task forces center on the R&D of specific PEC materials classes, others focus on critical activities to advance the supporting science and technologies in the PEC tool-chest. Important activities in the latter category include:

- Development of standardized testing and reporting protocols for evaluating candidate PEC materials systems on a level playing-field. In the past, the lack of standardized conditions and procedures for reporting PEC results has greatly hampered research progress across the board. To date, the Standardized Testing Task Force, which is being coordinated by the National Renewable Energy Laboratory (NREL), has made significant initial progress, recently drafting 18 detailed testing protocol documents that are under continued refinement for near term publication [6].
- Development and refinement of techno-economic analyses of PEC hydrogen production systems incorporating performance and processing cost feedback from the broader materials R&D efforts. The objective is to provide a basis for evaluating the long-term feasibility of large-scale PEC production technologies in comparison with other renewable approaches. Techno-economic analysis activities with the Working Group have been coordinated through Directed Technologies Incorporated [7].
- Development of advanced characterization techniques to enhance understanding of PEC materials and interfaces and promote breakthrough discoveries [8]. The materials characterization efforts employ the most advanced microstructural, optoelectronic, and electrochemical characterization techniques available to paint a comprehensive picture of the materials properties in relation to PEC performance. Example techniques include X-ray photoelectron spectroscopy, ultraviolet photoelectron spectroscopy, Auger, inverse photoemission spectroscopy, in ex situ as well as new, advanced in situ methods. Figure 2 shows the materials characterization facility developed at the University of Nevada, Las Vegas (UNLV), which is

FIGURE 2. Advanced Solid-State/Surface Characterization Tool at UNLV

a cornerstone of the PEC research characterization activities.

- Development of new theoretical models of PEC materials and interfaces critical to the design and engineering of new semiconductor systems [9]. For PEC semiconductor materials, the effects of impurity incorporation and other asymmetries on the band structures need to be calculated using both traditional and enhanced density-functional theory algorithm. Developing these sophisticated models of band states and bandgap, including effects of surface, interfaces and grain-boundaries, has been initiated within the PEC Working Group at NREL and the Lawrence Livermore National Laboratory.
- Development and implementation of innovative synthesis techniques to facilitate the PEC materials discovery process [10] represent important Working Group research activities. A broad spectrum of chemical, electrochemical and physical deposition methods are being employed to tailor material compositions and properties at the University of Hawaii, the University of California, Santa Barbara, and MVSsystems, Incorporated, for example. Additionally, rapid throughput combinatorial methods based on the different synthesis routes are being explored. Innovative synthesis routes can make or break the viability of a semiconductor system, a fact well-appreciated by the PV community.
- Development of standardized screening procedures for the “Up-Selection” and “Down-Selection” of DOE-supported PEC materials classes. The screening procedures are being developed in close coordination with the standardized testing, advanced characterization, and materials-theory activities. A hierarchy of screening protocols, ranging from top level device performance to detailed measurement of performance limiting materials and interface properties, is being formulated within the Working Group, as illustrated in Figure 3. Standard and consistent application of the best available theoretical and experimental

FIGURE 3. Block Diagram of PEC Screening Hierarchy under Development by the DOE PEC Working Group

techniques to direct research efforts is the objective of this important Working Group activity.

In the PEC Working Group, continued feedback between the theory, synthesis, characterization and analysis is providing fundamental insights needed to promote technical breakthroughs in a broad spectrum of promising PEC materials classes. The Working Group has initiated a white paper approach to the organization and tracking of scientific research progress. For each material class under investigation, a white paper is maintained as a living document which concisely summarizes the benefits, barriers, research status and approaches for addressing the barriers, all closely tied to the new advancements in theory, synthesis and characterization concurrently under development. The white papers also maintain a record of active research participants as well as a database of references documenting past achievements. To date, white papers have been drafted for a number of key focus materials classes including:

- **Tungsten-Oxide and Related Modified Compounds** - Tungsten oxide, particularly in thin-film and nano-particle forms, has been a workhorse in PEC applications for years. It is inexpensive and stable, but its high bandgap (~2.6 eV) is limiting to PEC performance. Photocurrent densities of approximately 3 mA/cm² have been achieved [11], with STH efficiencies over 3% in tandem configurations. To break the performance barrier, current research is focused on reducing bandgap

through ion incorporation into the tungsten oxide structure [12], and further integration in multi-junction devices.

- **Iron-Oxide and Related Modified Compounds** - Iron-oxide is abundant, stable, inexpensive and has a near-ideal bandgap (~2.1 eV) for PEC applications. Unfortunately, its poor absorption, photo-carrier lifetime and transport properties have been prohibitive to practical water-splitting. Current research to overcome these barriers have been encouraging, with recent progress in thin films and nano-structured materials [13,14]. Iron-oxide in tandem configurations may also be of interest for practical solar water-splitting.
- **Amorphous Silicon Compounds, including Silicon Carbides and Nitrides** - Amorphous silicon compounds have recently demonstrated interesting performances in PEC applications [15,16]. The progress of this material class in PEC applications has benefitted from decades of research in the PV community. Technical barriers remain in PEC stability and interface properties, and electrolyte and surface modification studies could help overcome these barriers. With material and interface improvements, monolithically fabricated multi-junction devices using amorphous silicon compound films have practical appeal for PEC water splitting.
- **Copper Chalcopyrite Compounds** - Copper chalcopyrite thin films are among the best absorbers of solar energy. As a result, chalcopyrite alloys formed with copper and gallium, indium, sulfur and

selenium have been widely characterized in the PV world. A great advantage of this material class for PEC applications is the bandgap tailoring based on composition, with bandgaps ranging from 1.0 eV in CuInSe_2 to 1.6 eV in CuGaSe_2 , and up to 2.43 eV in CuGaS_2 [17]. The CuGaSe_2 bandgap is attractive for PEC applications. Photo-current densities exceeding 13 mA/cm^2 have been demonstrated with this material [18] in biased PEC cells. Stability, surface kinetics and surface energetics remain as barriers, but if research can successfully address these, high STH efficiency could be achievable in low-cost thin-film copper chalcopyrite systems.

- **Tungsten- and Molybdenum-Sulfide Nano-Structures** - As bulk materials, tungsten- and molybdenum-sulfides are excellent hydrogen catalysts, but their bandgaps (below 1.2 eV) are too low for PEC water-splitting. Quantum confinement using nano-structuring, however, can increase the bandgap up to 2.5 eV. Current studies in nanostructured MoS_2 are focused on stable synthesis routes and integration of the nano-structures into practical bulk PEC devices [19].
- **III-V Semiconductor Classes** - High-quality crystalline semiconductor compounds of gallium, indium, phosphorous and arsenic have been studied for decades. In PEC experiments to date, STH efficiencies between 12 and 16 percent have been demonstrated in GaInP_2 /GaAs hybrid tandem photocathodes [20]. High cost and limited durability are the barriers to practical PEC hydrogen production, and breakthroughs in synthesis and in surface stabilization are being pursued.

Although there is still much work ahead for achieving high-performance low-cost PEC hydrogen production, research in these promising candidate materials has seen significant recent progress. The reader is referred to the cited references and to the progress reports for all of the DOE PEC Working Group 2009 AMR presentations (i.e., the presentations listed in Figure 1) for detailed progress in the individual materials categories.

Conclusions and Future Directions

The U.S. Department of Energy's Working Group on PEC hydrogen production has taken a collaborative approach in the R&D of novel PEC material systems. This approach, incorporating a broad spectrum of state-of-the-art techniques in theory, synthesis, characterization and analysis, is proving invaluable in the identification and development of the most promising materials for practical PEC hydrogen production. Continued Working Group efforts in conjunction with expanded international collaborations are expected to greatly facilitate the discovery and

optimization of material systems and devices capable of meeting the DOE PEC hydrogen production targets. The current collaborative pathway is expected to greatly facilitate the discovery and optimization of material systems and device configurations capable of meeting the DOE PEC production targets. Specific future directions include:

- Continued Advancement of DOE PEC Working Group Efforts:
 - Further PEC “Tool-Chest” development efforts.
 - Standardization of materials and device testing protocols.
 - Refinement of materials selection and prioritization criteria.
- Continued Expansion of Collaboration Efforts, Nationally and Internationally:
 - DOE PEC Working Group expansion.
 - U.S.-led “International Energy Agency PEC Annex-26”.

The ultimate aim is to make the materials and device breakthroughs necessary for high-efficiency, low-cost PEC hydrogen production.

Special Recognitions & Awards/Patents Issued

1. 2008 DOE Hydrogen Program R&D Award for DOE PEC Working Group Efforts: E. Miller.
2. IEA-HIA PEC Annex-26 Operating Agent Appointment: E. Miller.

FY 2009 Publications/Presentations

The publication list of the U.S. DOE PEC Working Group Members is extensive. The reader is referred to the progress reports of the 2009 DOE AMR presentations of the Working Group Participants (including oral presentations PD 23, 24, 25, as well as poster presentations PDP 05, 06, 07, 08 and 09) for a comprehensive list of publications.

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II.H.2 Technoeconomic Boundary Analysis of Photoelectrochemical (PEC) Hydrogen Producing Systems

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Contract Number: DE-AD36-08GO28031

Project Start Date: May 9, 2008
Project End Date: June 30, 2009 (modification
in process to extend to August 31, 2009)

Objectives

- Develop conceptual designs of four system configurations to produce hydrogen (H_2) using photoelectrochemical (PEC) processes.
- Calculate capital costs, operating costs and feedstock costs for conceptual designs.
- Perform boundary level economic and technical analysis using the current state of technology and future predictions.
- Compute levelized hydrogen costs for conceptual design.
- Determine key factors affecting cost estimates and quantify necessary improvements in the technology and system performance.

Technical Barriers

This project addresses the following technical barriers from Section 3.1 - Hydrogen Production of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (AD) System Design and Evaluation
- (AE) Diurnal Operation Limitations

Technical Targets

This project is conducting systems engineering analysis for PEC H_2 production. These studies and their results support the accomplishment of Hydrogen Production section milestones from the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan, namely;

- **Milestone 30:** Update technoeconomic analysis on the projected technology.
- **Milestone 31:** Identify materials/systems with a 2.3-eV useable semiconductor bandgap, 8% plant solar-to-hydrogen efficiency, and projected durability of 1,000 hours.

Accomplishments

- Designed single bed 'baggie' reactor for colloidal suspension system producing H_2 and O_2 mixed at an expected price of \$1.89/kg H_2 .
- Designed dual-bed 'baggie' reactor for colloidal suspension system capable of producing separated H_2 at an expected price of \$3.56/kg H_2 .
- Designed PEC cell panel concept for system capable of producing H_2 at an expected price of \$10.20/kg H_2 .
- Designed a concentrator PEC system concept for a system capable of producing H_2 at an expected price of \$3.98/kg H_2 .
- Concluded that primary factors affecting hydrogen costs from these systems are photoelectrode efficiency, material costs, and lifetimes.

Introduction

Renewable resources such as solar, wind and biomass are ideal hydrogen feedstocks because of their sustainability and clean nature. This study focuses on PEC hydrogen production from sunlight using both colloidal photoparticle suspension and photoelectrode cell technologies. The project goal is to design reactor systems which capitalize on the hydrogen producing capabilities of these technologies and predict costs of H_2 plants, including gas compression and separation, for continuous gas production. Baseline analyses of four PEC systems were performed with a sensitivity analysis showing sensitivities to performance assumptions for equipment, materials, and design. Economic potential of each system was postulated and compared to DOE metrics.

This effort will inform the DOE of predicted costs of H_2 as produced by various PEC methods. In turn, DOE will better understand the potential of this technology for H_2 production and be better able to allocate future resources to the most promising H_2 production alternatives.

Approach

For each of the four PEC systems, this analysis defined hydrogen production characteristics, individual reactor designs, and balance-of-plant equipment. This information was used to compute capital costs and levelized hydrogen costs. The analysis leveraged concepts, reactor parameters, and material assumptions generated by the PEC Working Group. The analysis was based on developing a large plant size from several smaller modules. Each module was sized for 1 tonne/day (TPD) H_2 production with large quantities of similar components within a single module. Additional capital cost reductions as a result of increased purchase quantities are not likely thus, capital costs of larger plants increase linearly. Most of the cost benefit is gained in the initial increase in plant size so a 10 TPD plant size was chosen. All of the systems used condensers and pressure swing adsorber (PSA) units, as necessary, to separate the H_2 from the O_2 and water vapor present in the gas stream. For three of the systems, a compressor with intercoolers was needed to compress the reactor output gases.

A sensitivity analysis for each PEC system was conducted to examine the cost effect of three parameters, namely; efficiency, PEC particle or cell cost and particle or cell lifetime. Each of the systems and the parameter boundaries explored are listed in Table 1. Efficiency is defined as the solar-to-hydrogen conversion efficiency i.e., net hydrogen lower heating value divided by total solar energy input.

Results

1. The Single Bed system using colloidal particles has a 'baggie' transparent plastic tube design to contain the water/particle mix and the product gases. This system raised hazard issues as to the stoichiometric mix of H_2 and O_2 .
2. The Dual-Bed system using colloidal particles has a dual 'baggie' design, shown in Figure 1, using separate bags for H_2 and O_2 generation. The ion bridge between bags allows ion transport, but prevents gas bubble transport. The slurry is circulated through perforated pipes to promote mixing within the bed and across the bridge.
3. The PEC Panel system uses thin film multilayer photovoltaic (PV) components with water and gas manifolds, mounted on 1 m x 2 m fixed geometry

TABLE 1. Sensitivity Parameters and Boundary Conditions

Type 1 - Single Reactor Bed Colloidal Suspension System			
	Low Cost	Baseline	High Cost
Efficiency	20%	10%	5%
Particle Life	10 yr	5 yr	1 yr
Particle Cost	\$152/kg	\$304/kg	\$9120/kg
Type 2 - Dual Reactor Bed Colloidal Suspension System with Ion Bridge			
Efficiency	20%	10%	5%
Particle Life	10 yr	5 yr	1 yr
Particle Cost	\$152/kg	\$304/kg	\$9120/kg
Type 3 - Thin Film PV System with Fixed Positioning			
Efficiency	20%	10%	5%
PV Life	20 yr	10 yr	5 yr
PV Cost	\$40/m ²	\$100/m ²	\$200/m ²
Type 4 - Thin Film PV System with Tracking and Concentrators			
Efficiency	25%	15%	10%
PV Life	20 yr	10 yr	5 yr
PV Cost	\$40/m ²	\$100/m ²	\$200/m ²

FIGURE 1. Type 2 Reactor Bed Conceptual Design

panels. The PEC system for 1 TPD H_2 output contains 30,000 panels (60,000 m²).

4. The Concentrator PEC system uses solar collectors with a 10:1 concentration ratio steerable in azimuth and elevation. Each PEC receiver unit mounted on a collector uses a multilayer PV cell with water and gas manifolds and is operated at 300 psi to allow elimination of the compressor.

For the systems above, the feasibility, performance, capital cost, and resultant \$/kg H_2 were evaluated using each of the given sensitivities. Production costs are summarized in Table 2.

Conclusions and Future Directions

The analyses for Types 1 – 4 are essentially complete. Further work needs to be done on control system costs and other system cost details. This analysis

TABLE 2. H₂ Production Costs

Type 1		Type 2	
Baseline (10% efficiency, 5 year particle lifetime, \$304/kg particle cost)	\$ 1.89	Baseline (10% efficiency, 5 year particle lifetime, \$304 /kg particle cost)	\$ 3.56
5% efficiency	\$ 2.39	5% efficiency	\$ 7.63
20% efficiency	\$ 1.63	20% efficiency	\$ 2.02
1 year particle lifetime	\$ 2.00	1 year particle lifetime	\$ 3.71
10 year particle lifetime	\$ 1.88	10 year particle lifetime	\$ 3.49
\$152 particle cost	\$ 1.86	\$152 particle cost	\$ 3.48
\$9120 Particle cost	\$ 3.18	\$9120 Particle cost	\$ 5.74
Type 3		Type 4	
Baseline (10% efficiency, 10 year PV lifetime, \$100/m ² PV cost)	\$10.20	Baseline (15% efficiency, 10 year PV lifetime, \$100/m ² PV cost)	\$ 3.84
5% efficiency	\$19.39	10% efficiency	\$ 5.61
20% efficiency	\$ 5.61	25% efficiency	\$ 2.47
5 year particle lifetime	\$13.30	5 year particle lifetime	\$ 4.02
20 year particle lifetime	\$ 8.81	20 year particle lifetime	\$ 3.77
\$40/m ² PV cost	\$ 5.55	\$40/m ² PV cost	\$ 3.62
\$200/m ² PV cost	\$13.52	\$200/m ² PV cost	\$ 4.21

produced several key findings which are listed below about PEC systems and how they can be used to generate H₂.

Type 1 System Findings:

- The product gas in this system is a stoichiometric mixture of H₂ and O₂ which raises safety issues.
- Lowest predicted H₂ costs.
- Composite nanoparticles with requisite voltages yet to be demonstrated.
- Indeterminate life of particles.

Type 2 System Findings:

- Low H₂ costs.
- Ion transport issues.
- Composite nanoparticles with requisite voltages yet to be demonstrated.
- Indeterminate life of particles.

Type 3 System Findings:

- Highest H₂ costs – large areas of PV component.
- Relies on low cost thin film PV material.
- Lifetime issues due to corrosion.

Type 4 System Findings:

- Low H₂ costs.
- Increased efficiency possible with PV development, and high temperature operation.
- Lifetime issues due to corrosion.

Based on the aforementioned findings, future work recommendations for each system are listed.

Type 1 System Recommendations:

- Resolve H₂/O₂ mixture issues.
- Develop nanoparticles with requisite photovoltage.

Type 2 System Recommendations:

- Develop ion-bridge between beds.
- Develop ionic charge carriers (I, Br, Fe, etc.).
- Develop nanoparticles with requisite photovoltage.
- Develop water circulation system.

Type 3 System Recommendations:

- Delay development until ultra-low cost multi-layer PV realized.

Type 4 System Recommendations:

- Develop low cost composite structures.
- Develop high pressure PEC operation.
- Investigate concentrator ratio ~20.
- Investigate high temperature operations, to increase efficiency or lower voltage requirement.

FY 2009 Publications/Presentations

1. 2009 DOE Hydrogen Program Review - Washington, D.C. – May, 2009. Presentation PD# 23.
2. H₂ Production Tech Team Mtg – Las Vegas, NV – 21 January 2009. Status Presentation.
3. PEC Program Review Meeting. Honolulu, Hawaii – 18 October 2008. Status Presentation.

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II.H.3 Characterization of Materials for Photoelectrochemical Hydrogen Production (PEC)

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Contract Numbers: DE-FG36-03GO13062
and DE-AC36-99GO10337

Project Start Date: October 1, 2004

Project End Date: May 5, 2010

Objectives

Enhance the understanding of photoelectrochemical (PEC) materials and interfaces and promote breakthrough discoveries by:

- Utilizing and developing cutting-edge soft X-ray and electron spectroscopy characterization.
- Determining electronic and chemical structures of PEC candidate materials.
- Addressing materials performance, materials lifetime, and capital costs through close collaboration with partners from the PEC working group.

Technical Barriers

This project addresses the following technical barriers from the Production section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (Y) Materials Efficiency
- (Z) Materials Durability
- (AD) Systems Design and Evaluation

Technical Targets

- Collaborate closely with partners within the DOE PEC working group to determine the electronic and chemical structure of candidate materials for solar water splitting.

- Aid the collaboration partners in the development/modification of novel candidate materials.
- Monitor deliberately introduced modifications of PEC candidate materials in view of the electronic and chemical structure.

Accomplishments

- Experimental determination of complete electronic surface structure of WO_3 and the impact of Mo doping/alloying in order to understand improved performance by a $\text{WO}_3\text{:Mo}/\text{WO}_3$ bilayer structure (with the University of Hawaii/Hawaii Natural Energy Institute, HNEI).
- Determination of the band gap of a-SiC and its change after oxygen/nitrogen exposure, hydrofluorhydric acid (HF) treatment, and/or annealing (with MVSystems).
- Investigation of the chemical composition and stability of ZnO, and particularly, the deliberate modification of the electronic structure through nitrogen incorporation (with the National Renewable Energy Laboratory, NREL).
- Comparison of PEC-tested and untested CuGaSe_2 samples (with the University of Hawaii/HNEI and NREL).
- Investigation of Fe_2O_3 thin films (with University of California, Santa Barbara).

Introduction

This project is embedded into the Department of Energy's efforts to develop materials for PEC water splitting. If successful, PEC will provide an important route to convert the energy supplied by solar irradiation into a transportable fuel. In order to achieve this goal, suitable materials need to be developed that simultaneously fulfill several requirements, among them chemical stability and optimized electronic structure, both for absorption of the solar spectrum and for electrochemical water splitting at a solid/electrolyte interface. This project experimentally derives the chemical and electronic structure information to (a) judge the suitability of a candidate material, (b) show pathways towards a deliberate optimization of a specific material, and (c) monitor whether deliberate modifications of the material indeed lead to the desired changes in electronic and chemical structure.

Approach

A unique “tool chest” of experimental techniques is utilized that allows to address all technical barriers related to electronic and chemical properties of various candidate materials. With these techniques it is possible to measure surface and bulk band gaps, the energy level alignment at interfaces, the chemical stability of the materials, and the impact of alloying and doping.

The tool chest includes photoelectron spectroscopy with X-ray and ultraviolet (UPS) excitation to determine the occupied electronic states (core levels and valence electrons) and inverse photoemission (IPES) to determine the unoccupied electronic states. These techniques, performed in the lab at UNLV, are surface-sensitive and allow a complete determination of the electronic and chemical *surface* structure. They are complemented by X-ray emission (XES) and X-ray absorption spectroscopy (XAS), performed at Beamline 8.0 of the Advanced Light Source, Lawrence Berkeley National Laboratory. XES and XAS also probe the occupied and unoccupied electronic states, but with a larger information depth. Furthermore, they also give insight into the chemical structure, again complementary to the electron-based techniques performed in the lab at UNLV.

Results

In collaboration with our partners, we have investigated numerous sample series on a variety of PEC candidate materials.

With the University of Hawaii/HNEI, we have determined the electronic level alignment of WO_3 thin film surfaces, as shown in Figure 1. Great care had to be taken to minimize radiation damage effects [1], and the data in Figure 1 represents such a “pristine” measurement series. From the shown UPS and IPES spectra, it is possible to derive a complete picture of the electronic structure at the sample surface, including the positions of valence band maximum and conduction band minimum, Fermi energy, and vacuum level/work function. Apart from establishing the benchmark picture of the electronic surface structure of WO_3 , one of the main goals was to elucidate the impact of Mo incorporation on the electronic surface properties. The results are shown in Figure 2, where the complete electronic surface structure of WO_3 (left) and $\text{WO}_3\text{:Mo}$ (right) is compared. Close inspection of the schematics reveals an upward shift of the vacuum level with respect to the Fermi energy, indicative of an increased work function for $\text{WO}_3\text{:Mo}$. Consequently, the alignment of the band edges is shifted with respect to the redox potentials responsible for water splitting. Furthermore, the upward shift of the band edges suggests that a $\text{WO}_3\text{:Mo}/\text{WO}_3$ bilayer structure, which has shown improved current collection with respect to both bulk materials ($\text{WO}_3\text{:Mo}$ and WO_3) [2], might possess an

FIGURE 1. UPS and IPES spectra of a WO_3 surface, together with the secondary electron (SE) cut-off measured by UPS. The linear extrapolations of the edges give the positions of the valence band minimum (VBM), the conduction band minimum (CBM), and the vacuum level (VL), respectively, as schematically shown below the panel. Error bars are ± 0.10 eV for the VBM and CBM positions, ± 0.14 eV for the derived electronic surface band gap, and ± 0.05 eV for the VL (work function).

additional electrostatic field at the interface, enhancing the charge carrier separation upon solar irradiation.

With our partners in Hawaii and at NREL, we have investigated CuGaSe_2 chalcopyrite thin film materials before and after PEC testing. For these studies, we have performed XES and XAS experiments to elucidate the chemical impact of PEC testing on these surfaces. Data analysis is currently in progress.

With our partners at MVSystems, we have conducted a variety of experiments to study the chemical surface structure and the associated electronic properties of a-SiC thin films. Figure 3 shows an example of this study. In the left panel, XES (black) and XAS (red) experiments are shown and analyzed to derive the electronic bulk band gap near the surface (note that the given value is a lower bound due to the potential presence of a core excitation in the XAS spectrum). The observed band gap of 3.3 eV is in good agreement with that found by our surface-sensitive techniques (after suitable surface cleaning). This is shown in the right panel of Figure 3, where UPS (left)

FIGURE 2. Positions of VBM and CBM of WO_3 and $\text{WO}_3:\text{Mo}$ relative to E_F , E_{vacuum} , and the normal hydrogen electrode (NHE). For comparison, the $\text{H}_2\text{O}/\text{O}_2$ oxidation and the H^+/H_2 reduction potentials are given. Grey bars for VBM and CBM indicate the error bars along the energy axis.

FIGURE 3. Valence and conduction band extrema of a-SiC, together with the derived band gap. Left: XAS (black) and XES (red) data to derive the band gap near surface (in the presence of a core hole). Right: UPS (left two curves) and IPES (right two curves) before (black) and after (red) HF treatment to derive the surface band gap.

and IPES (right) spectra are shown; spectra were taken before (black) and after (red) an HF etch treatment. Due to the high surface sensitivity of the UPS and IPES techniques, the surface band gap of the untreated sample is significantly enlarged (due to silicon oxide formation at the surface). In contrast, the HF etch treatment removes

silicon oxide from the surface and consequently also reduces the band gap value found at the surface.

With our partners at University of California, Santa Barbara, we have begun to investigate Fe_2O_3 thin films, in particular in view of the electronic band gap at the surface. Experiments are ongoing and will be described in the next report.

FIGURE 4. (a) O K XES spectra of a ZnO:N sample set with varying RF sputter power (i.e., varying N content). (b) Detailed presentation of features C and D (0-120 W), ascribed to Zn 3d states decaying into the O 1s core hole and to Zn L_2 emission (detected in 2nd order of the spectrometer and excited by higher orders of the beamline), respectively. (c) Detailed presentation of the valence band onset at high emission energies (0-120 W), indicating a shift of the valence band maximum.

With our partners at NREL, we have studied the suitability of ZnO and ZnO:N thin films for PEC applications [3]. As an example, Figure 4a shows O K XES spectra of a ZnO:N sample set with varying radio frequency sputter power (i.e., varying N content). The spectra contain a wealth of information about the chemical and electronic bulk structure near the surface. For example, the features C and D (Figure 4b) are ascribed to Zn 3d states decaying into the O 1s core hole and to Zn L_2 emission, respectively, and thus allow a quantitative analysis of the chemical environment of Zn, N, and O atoms. Furthermore, a detailed look at the valence band onset at high emission energies (Figure 4c), indicates a shift of the valence band maximum, while no significant shift in the XAS-derived conduction band minimum is found. This indicates that (a) the band gap is indeed reduced by the incorporation of N, and that (b) the main shift responsible for this reduction is found in the valence band (and not the conduction band). Further studies revealed that ZnO:N is stable when stored under vacuum conditions, but reverts back to ZnO when stored in air for longer periods of time.

Conclusions and Future Directions

- Established excellent collaboration structures with a large number of partners within the DOE PEC working group.

- Evaluated a variety of PEC candidate materials in view of their electronic and chemical properties.
- Developed the spectroscopic “tool chest” to give comprehensive picture of the electronic and chemical structure.
- Continue the collaborations with our existing partners and bring new partners “on-board” (e.g., Stanford University, studying tungsten and/or molybdenum dichalcogenide nanoclusters).
- Continue to determine electronic and chemical properties of various PEC candidate materials manufactured by the collaboration partners within the DOE PEC working group.
- Continue to improve the currently available experimental approaches.

FY 2009 Publications/Presentations

- “Electronic surface level positions of WO_3 thin films for photoelectrochemical hydrogen production”, L. Weinhardt, M. Blum, M. Bär, C. Heske, B. Cole, B. Marsen, and E.L. Miller, *J. Phys. Chem. C* **112**, 3078-3082 (2008).
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- C. Heske, “How soft x-ray spectroscopy can help the ‘Hydrogen Economy’ (hopefully)”, Seminar Experimentelle Physik II, University of Würzburg, Germany, July 8, 2008 (invited).
- “Spectroscopic characterization of thin films used in energy conversion devices”, M. Bär, 2008 American Chemical Society Western Regional Meeting, Las Vegas, Sept. 24–27, 2008 (Invited Oral).
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II.H.4 Nanostructured MoS₂ and WS₂ for the Solar Production of Hydrogen

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Objectives

Develop novel nanostructured dichalcogenide materials for photoelectrochemical (PEC) production of hydrogen from water:

- Synthesize nanometer-scaled MoS₂ and WS₂ as (1) nanoparticles, (2) nanowires, and (3) a 3-dimensional bi-continuous network.
- Explore and optimize bandgap and band edge position as a function of size and architecture for water splitting.
- Study photogenerated charge separation and transport in nanostructured materials.
- Investigate catalytic ability for water splitting as a function of surface structure.
- Incorporate optimized nanostructures into a PEC device and determine efficiency and durability.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section of the Hydrogen, Fuel Cells and Infrastructure Technologies (HFCIT) Program Multi-Year Research, Development and Demonstration (RD&D) Plan:

- (Y) Materials Efficiency
- (Z) Materials Durability
- (AB) Bulk Materials Synthesis
- (AC) Device Configuration Designs

Technical Targets

The focus of this project is the development of semiconductor materials with strong solar absorption characteristics that efficiently store energy from the sun by splitting water into hydrogen and oxygen. If successful, this project will address the following DOE technical targets as outlined in the HFCIT Multi-Year RD&D Plan:

TABLE 1. Progress towards Meeting Technical Targets for PEC Hydrogen Production

Characteristics	Units	2013 Target	2009 Status
Usable semiconductor bandgap	eV	2.3	1.9
Chemical conversion process efficiency (EC)	%	10	TBD
Plant solar-to-hydrogen efficiency (STH)	%	8	TBD
Plant durability	hr	1,000	TBD

TBD - to be determined

Accomplishments

- Optimized low temperature (150°C) sulfidization of MoO₃.
- Synthesized air-stable nanoscaled MoS₂ nanoparticles in various sizes.
- Achieved quantum confinement of MoS₂ nanoparticles with indirect bandgaps between 1.2–1.9 eV and direct bandgaps between 2.0–2.8 eV.
- Produced p-type MoS₂ to improve PEC stability.
- Produced highly stable RuO₂ counter electrodes for facile oxygen evolution with ~10% performance decrease over 100 cycles at 2 V vs. Ag/AgCl in a 0.1 M H₂SO₄ solution.
- Developed nanoscaled alumina templates for nanowire synthesis with mean pore diameter of 13 nm.

Introduction

PEC water splitting for hydrogen production was first demonstrated by Fujishima and Honda in 1972 using titanium dioxide (TiO₂) [1], a material limited to a maximum solar-to-hydrogen efficiency of 1% due to its large bandgap of 3.0 eV. Since the maximum solar-to-hydrogen efficiency of a material is ultimately determined by its ability to absorb light, research efforts

have primarily focused on improving solar absorption characteristics, including the use of semiconductor doping/alloying [2-6], tandem absorbers [7,8], and dye sensitization [9,10]. However, even the best absorbers to date are compounded by problems following the initial absorption such as poor charge transport and/or poor stability [11,12]. Thus, no material system exists that can yet be considered as a wide-scale deployable solution. The world record device with 12.4% solar-to-hydrogen efficiency was developed by Khaselev and Turner over a decade ago in 1998 [13], but exhibited significant stability problems and extremely high cost [14,15]. New approaches are necessary to accelerate the development of highly efficient, durable, and low cost materials for PEC water splitting.

Approach

The project discussed here aims to improve upon previous material deficiencies through the nanostructuring of low cost semiconductor materials – in particular, molybdenum disulfide (MoS_2) and tungsten disulfide (WS_2). Both materials exhibit a bandgap of ~ 1.2 eV [16-19], which enables the absorption of a significant portion of the solar spectrum. However, this value is too small to provide the photovoltage necessary to drive the water splitting reaction ($\Delta G = 1.23$ eV). The minimum bandgap must encompass that thermodynamic water splitting potential of 1.23 eV in addition to the activation energies required to drive the individual hydrogen and oxygen evolution half reactions. Thus, the optimal bandgap value will likely lie in the range of ~ 1.8 -2.0 eV [20]. Nanostructuring materials can result in an effect known as quantum confinement [19,21,22], which enables widening of the bandgap to a larger, more useable value for water splitting in the case of MoS_2 and WS_2 . In addition, edge sites at the surface of MoS_2 , which are more prominent when nanostructured, have been documented as centers of high catalytic activity for the hydrogen evolution reaction [23]. This translates into a smaller required bandgap and higher theoretical efficiency.

Lastly, controlling the type of conductivity has important consequences on the material's photoelectrochemical properties. By focusing on synthesizing p-type (rather than n-type) MoS_2 and WS_2 , the possibility of photo-oxidation is minimized and stability can be improved since the material operates as a photocathode and oxidizing holes flow away from the semiconductor-electrolyte interface [24-28].

Results

Our efforts within the first six months of the project have focused on the development of MoS_2 , since it represents a material with a rich history of catalysis and photoactivity [22,29-31]. We have optimized the sulfidization of molybdenum in our laboratory using temperatures as low as 150°C , confirmed using ultraviolet-visible transmission (UV-Vis) spectroscopy and X-ray photoelectron spectroscopy (XPS). Electrochemical testing of MoS_2 also revealed high activity for the hydrogen evolution reaction, in agreement with previous reports [23].

Synthesis of supported MoS_2 nanoparticles in various sizes was accomplished using a reverse micelle encapsulation method [32-34]. The low temperature sulfidization process minimized nanoparticle sintering. The nanoparticles were imaged using atomic force microscopy (AFM) as shown in Figure 1, although exact size measurements are limited due to convolution of the AFM tip. Work is currently underway to precisely determination the size distributions of such nanoparticles using transmission electron microscopy. Despite their small size, these nanoparticles are fully resistant to oxidation from exposure to air, as confirmed using XPS.

UV-Vis spectroscopy of the MoS_2 nanoparticles revealed a blue-shift in their absorption onset. Furthermore, the degree of blue-shifting increased with smaller nanoparticle size. This behavior is expected and is characteristic of the quantum confinement phenomenon. Tauc plots of the direct and indirect bandgaps are shown in Figure 2.

FIGURE 1. Atomic force microscopy of MoS_2 nanoparticles in increasing size from (a)→(d), produced using an inverse micelle encapsulation method, using a poly(styrene-*b*-2-vinylpyridine) polymer and a MoCl_3 precursor.

FIGURE 2. MoS₂ absorption shown in (a) allowed indirect and (b) allowed direct Tauc plots. Bulk MoS₂ films show an indirect bandgap of ~ 1.2 eV and a direct bandgap of ~ 2.0 eV (green circles). MoS₂ nanoparticles from Figure 1(d) show an indirect bandgap of ~ 1.5 eV and a direct bandgap of ~ 2.5 eV (blue triangles), while nanoparticles from Figure 1(c) show an indirect bandgap of ~ 1.9 eV and a direct bandgap of ~ 2.8 eV (red squares).

While MoS₂ crystals in nature can be found to have either n-type or p-type conductivity, we have synthesized consistently p-type MoS₂ by the addition of Nb. Conductivity type was assessed using photocurrent measurements under an applied bias in an electrochemical cell, shown in Figure 3. The observed photocurrent was negative in sign, and increased towards negative potentials, characteristic of p-type behavior.

As part of the effort to develop p-type MoS₂, it is necessary to produce counter-electrodes that have low overpotentials for the oxygen evolution reaction. RuO₂ is a material that exhibits high conductivity, chemical and thermal stability, and catalytic activity [35-37]. Using an electrochemical deposition technique followed by a heat treatment, we produced RuO₂ counter-electrodes that exhibit a 400 mV earlier onset for oxygen

FIGURE 3. PEC response for Nb-doped MoS₂ thin film under chopped illumination from a ~ 2.5 Sun xenon lamp.

FIGURE 4. (a) Cyclic voltammogram of oxygen evolution reaction for a RuO₂ electrode (solid line) compared to a Pt electrode (dotted line). (b) Stability of RuO₂ electrodes unannealed and annealed at 400°C for 1 hr during 100 cyclic voltammograms between 0.5 V up to 1.5 V or 2.0 V vs. Ag/AgCl.

evolution compared to Pt as shown in Figure 4(a), and demonstrates strong stability over 100 cycles of oxygen evolution, even when subjected to a +2 V bias vs. the Ag/AgCl reference electrode in a highly acidic 0.1 M H_2SO_4 solution as shown in Figure 4(b).

Our efforts to synthesize nanowires have been focused on the development of anodic alumina templates [38-42]. We have achieved the synthesis of templates with 13 nm pores, as imaged by scanning electron microscopy, and are continuing to optimize the synthesis towards even smaller pore sizes. We have also synthesized samples of the bi-continuous network templates using a silica template [43-45] and are continuing with further development. Following the development of these templates, we will synthesize molybdenum and tungsten nanostructures using an electrodeposition process that we optimized in our laboratory.

Conclusions and Future Directions

We have made significant process in developing nanostructured MoS_2 for PEC water splitting:

- Optimized low temperature sulfidization of molybdenum.
- Synthesized air stable nanoparticulate MoS_2 in various sizes.
- Confirmed size-dependent quantum confinement of nanoparticulate MoS_2 , widening the bandgap to values of ~ 2 eV.
- Synthesized p-type MoS_2 .
- Developed anodic alumina templates with nanopores.

Our work on this project continues with the assessment of the valence and conduction band edges of our nanostructured MoS_2 , using spectroscopic techniques such as ultraviolet photoelectron spectroscopy coupled to inverse photoemission spectroscopy. We plan to assess the flat band potential using electrochemical techniques such as illuminated open circuit potential, Mott-Schottky, and photocurrent onset. This will enable determination of the surface electronic structure of our semiconductor materials and provide insight into their ability to actively split water using sunlight without an applied bias. We will also pursue PEC measurements on the supported nanostructures, measuring photocurrent with and without an applied bias and sampling the gas headspace by gas chromatography.

Work is underway to further develop the anodic alumina templates, as well as the nanoporous bi-continuous networks. The templates will enable the development of MoS_2 and WS_2 nanowires and bi-continuous networks using an electrodeposition process.

Although initial efforts have focused on MoS_2 , work is already underway to develop WS_2 nanostructures. WS_2 is an important avenue of study due to its structural and electronic similarities to MoS_2 . By studying both MoS_2 and WS_2 in multiple nanostructured forms, we address the challenge of developing a deployable PEC water splitting device using state-of-the-art techniques, with significant potential for producing knowledge that spans a large number of scientific fields, including photovoltaics and heterogeneous catalysis.

FY 2009 Presentations

1. 2009 US DOE Hydrogen Program and Vehicle Technologies Annual Merit Review & Peer Evaluation Meeting, Arlington, VA. "Nanostructured MoS_2 and WS_2 for the solar production of hydrogen" T.F. Jaramillo, May 2009.
2. US DOE Photoelectrochemical Hydrogen Production Quarterly Meeting, San Francisco, CA. "Nanostructured MoS_2 and WS_2 for the solar production of hydrogen" T.F. Jaramillo, April 2009.
3. University of California, Berkeley, Nanosciences and Nanoengineering Institute (BNNI), Nanoscale Science and Engineering (NSE) Seminar, Berkeley, CA. "Designing nano-scaled, non-precious metal catalysts for hydrogen evolution" T.F. Jaramillo, March 2009.
4. Chevron Corporation, Richmond, CA, May 2009. "Solar Fuels by Photoelectrochemistry (PEC)" T.F. Jaramillo, March 2009.
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II.H.5 Photoelectrochemical Hydrogen Production Using New Combinatorial Chemistry Derived Materials

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Contract Number: DE-FG36-05GO15040

Project Start Date: September 1, 2004
Project End Date: December 31, 2009

Objectives

- A focus on the use of abundant and non-toxic elements in the development of improved photoelectrocatalyst (PEC) materials for the capture of solar radiation to catalyze chemical reactions of interest.
- Utilize high-throughput screening to identify candidate materials that, with optimization, might meet the DOE performance and stability targets.
- Explore the effects of morphology on the PEC material system efficiency making use of nanostructures to minimize charge carrier path lengths and maximize reactive surface area.
- Explore processing and synthesis parameters to optimize efficiency through increased conductivity and minimized charge trapping and surface recombination of selected materials.
- Continue synthesis of libraries of semiconductor heterostructures for improved charge separation efficiency and/or stability.
- Use of GHz and THz photoconductivity as a tool to understand the photoresponse and carrier dynamics of semiconducting PEC materials.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (Y) Materials Efficiency
- (Z) Materials Durability
- (AA) PEC Device and System Auxiliary Material
- (AB) Bulk Materials Synthesis

Technical Targets

Characteristics	Units	2003 Target	2007 Target	Achieved 2008	2013 Target
Usable semiconductor bandgap	eV	2.8	2.1	2.1	2.3
Chemical conversion process efficiency (EC)	%	4	1	1	10
Plant solar-to-hydrogen (STH) efficiency	%	NA	NA	NA	8
Plant durability	hr	NA	<100	<100	1,000

NA - not applicable

Accomplishments

- Exploration of iron oxide electrodes with different levels of dopants made by electrodeposition.
- Explored the effect of poly-alcohols as alternate organic electron donors.
- Investigated surface processing for band edge position shift and electrocatalysis.
- Developed a spray pyrolysis synthesis system for hematite thin films with controlled Ti and Si doping.
- Developed a photoelectrochemical reactor and hydrogen production measurement system for colloidal photocatalysts.
- Designed and explore the synthesis of mesoporous and nanostructured delafossite and chalcogenide semiconductors.

Introduction

The overall project objective is to discover and optimize an efficient, practical, and economically sustainable material for photoelectrochemical production of bulk hydrogen from water – a clean, renewable route to hydrogen energy. The properties of the semiconductors investigated for this application, which are similar to those in photovoltaic devices, must satisfy conditions in several areas if cost-effective hydrogen production is to be realized: (1) efficient solar absorption, (2) effective charge separation/transport, (3) appropriate conduction band/valence band energies relative to H_2 and O_2 redox potentials (“band matching”), (4) facile interfacial charge transfer, (5) long-term stability, and (6) low cost. A material which satisfies all the above conditions simultaneously could provide clean hydrogen in bulk and at low cost; unfortunately, no such material or system has been discovered or developed to date. The DOE has identified the following future targets for STH efficiency and durability: 2006, 4%; 2013, 8% and 1,000 hrs; 2018, 10% and 5,000 hrs.

Hematite ($\alpha\text{-Fe}_2\text{O}_3$) has many potential advantages for hydrogen photoproduction. It has a bandgap of 2.2 eV (absorbs approximately 40% of the solar spectrum), it is stable in electrolytes over a wide range of pHs and is abundant, inexpensive and non-toxic [1-3]. Several qualities have limited the use of this material as an efficient photocatalyst, including high electrical resistance and recombination rates of photogenerated electrons [4,5] and a conduction surface band-edge that is lower than the redox level of H^+/H_2 . The undesirable electrical properties are partially due to the hopping mechanism of charge transfer via oxygen vacancies, grain boundaries, and surface traps, which results in relatively low quantum yields, while the low conduction band is due to the Fe 3d electrons. Efforts have been devoted to reducing the resistivity of thin films by nanostructured crystal engineering, that is; electron transport along the (001) planes of the hematite has four orders or magnitude lower resistance than transport perpendicular to this plane. Our hypothesis is that by deliberately doping hematite with selected heteroatoms [6] and being able to control the growth dimensions, crystal orientation and facets exposed, these limitations may be overcome. There is much diversity to explore in searching for the appropriate combination of dopant species to improve photocatalytic performance, [5,8-10] as well as to understand and engineer the crystal structure, orientation and size of the crystalline domains of hematite. Another approach is to modify the surface reaction of semiconductors, through band edge shift, surface electrocatalyst deposition, and alternate poly-alcohol as electron donors, to further improve the performance of photocatalysts.

Approach

The approach of this project involves the application of combinatorial chemistry methods to synthesize and optimize PEC materials and systems for cost-effective hydrogen production. This represents a systematic and high-speed exploration of new metal-oxide based solid-state materials. Our approach focuses upon the investigation of semiconductor materials that are inherently inexpensive, such as iron oxide. Iron oxide materials can be synthesized by rapid serial electrodeposition techniques or can be synthesized by sol-gel or spray pyrolysis, however, the limiting step in this case is still the high-throughput screening of materials, thus by utilizing the high-throughput screening system we can expedite the material discovery. By investigating large arrays of diverse doped hematite films, we are working to improve the understanding of the fundamental mechanisms and composition-structure-property relationships within these systems. Surface modification has been attempted to shift the flat band potential of doped hematite and to increase the zero bias photocurrent. New hydrogen producing photocatalysts were synthesized and characterized using the PEC reactor and hydrogen production measurement system.

Results

The automated electrochemical synthesis system has been designed and improved allowing using electrodeposition for a variety of new materials with program controls over electrochemical parameters like voltage, scan rate, cycle numbers, etc. We have focused mainly on Fe_2O_3 host, investigating libraries of variable composition and structure. $\alpha\text{-Fe}_2\text{O}_3$ thin films with different dopants have been synthesized by co-electrodeposition techniques. Around 30 dopants such as Al, Zn, Cu, Ni, Co, Cr, Mo, Ti, Pt, etc. were investigated. Doping with Al, Ti, Pt, Cr, and Mo exhibits the most promising results. Here we show the results of Al, Cr, and Mo doping in Figure 1. Besides their PEC performances, the phases, morphologies, optical properties and elemental components of the doped iron oxide thin films have also been characterized by X-ray diffraction, scanning electron microscopy, ultraviolet-visible, and X-ray photoelectron spectroscopy. Upon doping, the microstructures of the films varied; however, no preferred crystallographic orientation or dopant phase segregation was observed. There was only a small difference in the absorption properties of doped and undoped samples, which is mainly due to the variations in the sample thickness and morphologically dependent scattering of the films. Figure 1a, b and c show the photocurrent and incident photon conversion efficiency (IPCE) of Cr and Mo doped hematite thin films. The best performing samples were 5% Cr and 15% Mo doped which had IPCEs at 400 nm of 6% and 12%, respectively, with an

FIGURE 1. IV curves of (a) Cr doping and (b) Mo doping at 410 mW/cm² illumination. Inset shows magnification of origin. (c) IPCE of the electrodeposited films with and without doping at different applied potentials in N₂ degassed 1 M NaOH. (d) IV-Curves of control sample and Al doped samples (e) IPCE of selected samples at 0.2 and 0.4 V vs. Ag/AgCl.

applied potential of 0.4V vs. Ag/AgCl. These IPCE values were 2.2× and 4× higher than the undoped sample for the 5% Cr and 15% Mo samples, respectively. The chopped current-voltage (IV) curves for Al doped iron oxide thin films, Figure 1d, show the best performance with 10% of Al in the electrolyte bath. The 10% Al in the electrolyte bath, which corresponds to a 0.3-0.5% doping, gives the IPCE at 400 nm of 8%. The increase in performance is attributed to an improvement in the charge transport properties within the films and not due to significant

changes in the electrocatalytic rates due to dopants residing at the surface.

The doping of heteroatoms has been shown to increase the conductivity of hematite by orders of magnitude and thus the PEC performance on water splitting. However, the energy of the conduction band relative to the redox level of the H₂/H⁺ couple is too low (~0.2 V vs. the normal hydrogen electrode) to efficiently drive the hydrogen evolution reaction. Therefore, all

publications with hematite require an external bias to shift the conduction band position above the hydrogen evolution potential. We have demonstrated an effective way to shift the band position of Ti doped hematite through surface modification using fluoride, which forms Ti-F bonds on surface. Figure 2 shows the improved PEC performance of Ti doped hematite thin films by CoF_3 (aqueous solution, pH~3.0) treatment. The CoF_3 treated samples show improvement in photocurrent at low bias ($V < 0.3$ V vs. Ag/AgCl). The photocurrent onset potential for the treated sample is lower (~ 0.2 V) than the control sample. Furthermore, the untreated sample shows a negligible photocurrent at zero bias measured between the sample photoanode and the Pt mesh counter electrode without a reference electrode whereas a CoF_3 aqueous solution treated sample shows a photocurrent of approximately 150 mA/cm^2 under identical conditions and remains stable for more than 3,000 s (see Figure 2c). We propose that, the flat-band potential of the sample is more negatively shifted after CoF_3 treatment. This hypothesis is confirmed by the Mott-Schottky analysis, which shows a negative shift of ~ 0.15 V for the treated sample. When glucose was

used as the electron donor, the photocurrent was further increased, as shown in Figures 2b, c and d, which is consistent with the slower rate for the oxygen evolution reaction of water oxidation than for the oxidation of glucose. The IPCE of the fluoride treated sample with the presence of glucose at zero bias (only 2-electrode) reaches 3.7% at 400 nm with respect to 1.5% in the absence of glucose and 0.1% for control sample, Figure 2d.

The effect of water and carbon on the photoactivity of Ti doped hematite thin films was investigated by the use of pyrolysis of anhydrous precursors, Figure 3a. Using iron carbonyl and TiCl_4 precursors, faceted nanoparticles with an average size of about 20 nm were obtained on the fluorine-doped tin oxide substrates (Figure 3b) and a photocurrent of 1.2 mA/cm^2 was observed at 0.2 V vs. Ag/AgCl under visible light illumination of 100 mW/cm^2 (Figure 3c). The IPCE of the sample approaches 11.4% and 15.5% at 400 nm with an applied bias of 0.2 V and 0.4 V vs. Ag/AgCl, respectively, Figure 3d. The onset potential for photocurrent is approximately -0.4 V vs. Ag/AgCl. A higher zero biased photocurrent ($\sim 400 \text{ }\mu\text{A}$) is also

FIGURE 2. Chopped IV curves of 6% Ti-doped iron oxide thin films before and after CoF_3 aqueous solution treatment in N_2 degassed 1 M NaOH solution (a) without glucose and (b) with 10 mM glucose; (c) zero bias photocurrent under white light illumination for the same samples: (i) before and (ii) after CoF_3 aqueous solution treatment, (iii) after CoF_3 aqueous solution treatment in the presence of glucose in the electrolyte; and (d) IPCE performance at zero bias (i, ii, iii are the same as in (c)).

FIGURE 3. (a) Schematics of spray pyrolysis method for preparation of Ti doped hematite thin films; (b) scanning electron microscope image of Ti:Fe₂O₃ thin film sample prepared using TiCl₄ and Fe(CO)₅ precursors. (c) 3-electrode chopped IV curves showing the Ti:Fe₂O₃ sample under 100 and 403 mW/cm² visible light illumination and N₂ degassed 1 M NaOH; (d) IPCE for the Ti:Fe₂O₃ sample in N₂ degassed 1 M NaOH with 0.2 and 0.4 V applied bias vs. Ag/AgCl in 1 M NaOH solution.

observed for this sample. Different Ti precursors, e.g. aqueous TiCl₃ solution and Ti(butyloxy)₄, have been used for Ti doping, which results in a much lower efficiency. The control on dopant concentration, thickness, and crystalline growth orientation is under investigation. Surface modification using fluoride is in progress and a higher zero bias photocurrent (2-electrode) is expected.

A photoelectrochemical reaction and characterization system for colloidal photocatalysts was designed and applied for screening of new potential photocatalysts, Figure 4. Photocatalyst powders (~10 mg) were dispersed in 15 mL electrolyte and sealed by a septum in a 20 mL glass vial. The vials were illuminated in a PEC reactor by two 1,000 W light bulbs with infrared filters. The PEC reactors can hold nine vials and do a screening for them by injecting gas samples from headspace of the vials into gas chromatograph. This system has been applied in screening a variety of semiconductors (Figure 4b) in terms of their photoelectrocatalytic hydrogen production rate under visible light illumination. Several semiconductors have been shown to be active in hydrogen production under visible light illumination in basic Na₂S solution, such as CuCrO₂, CuGaO₂, CuLaO₂, CuGaSe₂, InP, etc.

Quantitative analysis and screening of electrolytes for each semiconductor are in progress and the results will be reported in the next annual report.

Conclusions and Future Directions

- The methodology of combinatorial material science has been applied to expedite the discovery of improved photocatalytic materials for hydrogen production.
- An automated electrochemical system has been used to reliably synthesize iron oxide thin films doped with various heteroatoms.
- The Al-, Ti-, Cr-, Mo-, and Pt-doped iron oxide thin films show a remarkable improvement in efficiency for photoelectrochemical water splitting compared to undoped samples.
- Surface modification by fluoride has been successfully applied to negatively shift the band-position of Ti doped hematite.
- Continue optimization of doped hematite; using theory to guide multi-atom substitutions in the α-Fe₂O₃ lattice, especially on both a donor and an acceptor co-doping.

FIGURE 4. (a) Schematics of photoelectrochemical reactor and hydrogen production measurement system using gas chromatograph. The PEC reactor includes two 1,000 W bulbs and two water tanks as infrared filter. Nine sample vials can be held on the turn table in the metal box. Sample powders were dispersed in the vial and purged with Ar before illumination. After illumination, 500 µL gas sample were obtained from the headspace of the vial and injected into a gas chromatograph for hydrogen concentration analysis. (b) Screening results of semiconductors on hydrogen production under visible light illumination. The concentration of NaOH + Na₂S electrolyte is 1 M NaOH and 0.025 M Na₂S. The concentration of HBr electrolyte is 0.025 M.

- High-throughput synthesis of electrocatalysts on α -Fe₂O₃ substrates compatible with electrolyte, and reactant/product properties.
- Heterostructure design and synthesis with high efficiency of charge carrier separation.
- Ti doped iron oxide nano/mesoporous particles synthesis and control over growth structure, and surface modification for direct water splitting.
- Exploration of other narrow bandgap semiconductors, delafossite alloy, phosphide, and chalcogenides.
- Single-sample slurry reactor for IQE measurement and quantitative H₂ analysis.

FY 2009 Publications/Presentations

1. A. Kleiman-Shwarscstein, Y.-S. Hu, G.D. Stucky and E.W. McFarland, "NiFe-oxide Electrocatalyst for the Improvement of Oxygen Evolution Reaction on Ti-doped Hematite Photoelectrodes", *Electrochemical Communication*, doi:10.1016/j.elecom.2009.03.034.

2. A. Kleiman-Shwarscstein, P. Zhang, Y.-S. Hu, E.W. McFarland, "Solar Hydrogen and Nanotechnology", Chapter 13, Vayssieres, L., Ed.; John Wiley & Sons, (to be published 8/09).

3. Y.-S. Hu, A. Kleiman-Shwarscstein, G.D. Stucky and E.W. McFarland, "Improved Photoelectrochemical Performance of Ti-doped α -Fe₂O₃ Thin Films by Surface Modification with Fluoride", *Chem. Comm.* 2009, 2652 - 2654 (doi: 10.1039/b901135h).

4. A. Kleiman-Shwarscstein, Y.-S. Hu, A. Forman, G.D. Stucky and E.W. McFarland, "Electrodeposition of α -Fe₂O₃ of doped with Mo and Cr and its application towards water splitting", *J. Phys Chem C*, 2008; 20(12); 3803-3805.

5. A. Kleiman-Shwarscstein, "Solar Hydrogen Production by Photo-oxidation of Water from Doped Iron Oxide Photoanodes" Talk, presented at ACS Annual Meeting, March 2009.

6. P. Zhang, "Nanostructured Cu(X)O₂ Delafossite Photoelectrocatalysts for Solar-to-Chemical Energy Conversion" Talk, presented at Materials Research Society, April 2009.

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II.H.6 Semiconductor Materials for Photoelectrolysis

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Projected End Date: Project continuation and
direction determined annually by DOE

Accomplishments

- Completed characterization of InGaN samples from Los Alamos National Laboratory (LANL) and determined water-splitting capabilities.
- Completed characterization of hot-wire chemical vapor deposited SiN.
- Completed preliminary characterization of a-SiN samples grown by MVSsystems, Inc., using plasma-enhanced chemical vapor deposition and found encouraging photocurrents under bias.
- Made progress in optimizing platinum catalyst treatments on CuGaSe₂ photoelectrodes.
- Synthesized and characterized nanocrystalline Co-Al-Fe oxide composite electrodes.
- Completed evaluation of Co-Fe-Al oxide materials and, as a result of poor electronic transport properties, decided against (No-Go) further study of this material class.

Objectives

- Identify, synthesize, and characterize new semiconductor materials that have the possibility of meeting the criteria for a viable photoelectrochemical (PEC) hydrogen-producing device.
- Design and synthesize multi-junction devices for high-efficiency water splitting.

Technical Barriers

This project addresses the following technical barriers from the Photoelectrochemical Hydrogen Production section of the Hydrogen, Fuel Cells, and Infrastructure Technologies Program Multi-Year Research, Development, and Demonstration Plan (MYPP):

- (Y) Materials Durability
- (Z) Materials Efficiency
- (AC) Device Configuration Designs

Technical Targets

The 2013 technical targets from the MYPP PEC hydrogen production goals are as follows:

- Bandgap of 2.3 eV.
- 10% chemical conversion process efficiency.
- 1,000-hour lifetime.

Introduction

PEC combines a light-harvesting system and a water-splitting system into a single monolithic device. A semiconductor immersed in aqueous solution comprises the light-harvesting system. The catalyzed surface of the semiconductor is one part of the water-splitting system, and the other part is another electrode in a separate compartment. The key is to find a semiconductor system that can efficiently and sustainably collect solar energy and direct it toward the water-splitting reaction.

The goal of this work is to discover and characterize a semiconductor material set or device configuration that (i) splits water into hydrogen and oxygen spontaneously upon illumination, (ii) has a solar-to-hydrogen efficiency of at least 5% with a clear pathway to a 10% water-splitting system, (iii) exhibits the possibility of 10 years of stability under solar conditions, and (iv) can be adapted to volume-manufacturing techniques.

Approach

- Perform semiconductor materials discovery and development for application to PEC water splitting.
- Employ a multifaceted approach to materials discovery that includes theoretical calculations to identify potentially promising candidates, synthesis of novel semiconductors, and characterization of their physical and photoelectrochemical properties.

- Feedback results for the next iteration of calculations.
- Characterize other unique materials obtained outside the theory-synthesis-characterization feedback loop.

While stability is important for viable PEC conversion devices, it cannot be the determining factor in choosing PEC material sets. The focus of research in the PEC community on (mainly) oxides for the last 30 years has produced no successes; efficiencies remain abysmally low. A new approach and methodology is warranted to explore new materials with the capability of reaching the efficiencies needed for commercial devices. One can then discuss approaches that can lead to the necessary lifetimes.

At present, metal oxides (in particular, TiO_2 , WO_3 , and Fe_2O_3) are considered primary candidates, however, none of them fulfills the requirements for a successful PEC material. Finding novel materials and approaches that promise to fulfill all the MYPP requirements in one material class would be a significant advance.

The current material sets used in commercial solar cells represent a relatively little-studied area for PEC research and are the focus of our materials study.

Results

Nitride Materials

InGaN is an emerging material that has the possibility of meeting the varied requirements for an efficient PEC device. InGaN is a challenging material to synthesize using conventional molecular beam epitaxy (MBE) techniques. High-quality material typically requires elevated substrate temperatures, which limits the incorporation of indium. Indium content is critical for lowering the bandgap into the visible region of the solar spectrum, a condition necessary for high-conversion efficiency. Conventional MBE uses a nitrogen plasma as the group V source. The modified MBE technique developed at LANL uses a high-energy laser to atomize nitrogen resulting in a semi-collimated beam of nitrogen atoms with energies between 1.5 eV and 2.0 eV. The advantage of using energetic atomic nitrogen as the reactive group V species is that the nitrogen atoms have an energy level around the activation energy necessary for nitride growth. This level allows high-quality materials to grow at lower temperatures, expanding the accessible InGaN compositional range. Indium can be used to tune both the bandgap and the band-edge positions at the electrolyte interface. The band-edge positions are critical as they define the reduction and oxidation photoreactions possible as well as the thermodynamic driving force available for them.

We obtained three compositions of $\text{In}_x\text{Ga}_{1-x}\text{N}$ grown at LANL using laser-assisted MBE. The nominal compositions of the LANL films are $\text{In}_{0.2}\text{Ga}_{0.8}\text{N}$, $\text{In}_{0.3}\text{Ga}_{0.7}\text{N}$, and $\text{In}_{0.35}\text{Ga}_{0.65}\text{N}$, and the resulting films appear yellow, orange, and red, respectively. We used photocurrent spectroscopy to determine the band gap energies to be 2.6 eV (yellow), 1.9 eV (orange), and 1.7 eV (red). Though they were grown undoped, the materials exhibited n-type conductivity. In order to photoelectrochemically split water, the flatband potential (V_{fb}) and the minority band edge, which for an n-type semiconductor is the valence band, must span the potentials of the hydrogen and oxygen evolution half-reactions. All three InGaN samples are n-type, so a V_{fb} slightly negative (above on the electrochemical scale) of the hydrogen potential would indicate the material can reduce water to H_2 . Because the Fermi level of n-type semiconductors is just below the conduction band, after adding the band gap energy, the valence band should be positive of the oxygen potential. We attempted to establish the positions of the band-edges by measuring the V_{fb} using Mott-Schottky analysis, illuminated open-circuit potential measurements and measurements of the photocurrent onset potential. Because band-edge positions and water-splitting potentials shift with pH, measurements were made in buffered solutions of pH 2, 6, and 10.

Mott-Schottky (M-S) analysis models the semiconductor/electrolyte interface as a simple series resistor-capacitor circuit and uses capacitance measurements of the depletion layer to establish the V_{fb} position. An M-S plot is the inverse of (depletion layer) capacitance squared versus the applied potential (versus reference). Under ideal conditions an M-S plot should have a linear portion that can fit with a trend line using linear regression; the x-intercept of the regression fit is the V_{fb} , and the slope is inversely proportional to the apparent dopant density. Illuminated open-circuit potential (OCP) measurements assume that under intense illumination the bands will flatten and the measured potential, versus a reference electrode potential, is the V_{fb} . Using three electrode current-potential measurements was another method to establish the V_{fb} positions. The potential where photocurrent commences is assumed to be the V_{fb} because the reverse bias is necessary to observe photocurrent (flatband and forward bias do not have an electric field at the semiconductor/electrolyte interface necessary for separating photogenerated carriers). The photocurrent is anodic for n-type semiconductors.

Flatband potential analyses to determine if the band-edge potentials spanned the decomposition potentials of water gave results that varied by technique (Figure 1). M-S analysis indicated the conduction band edge was above the hydrogen-evolution potential, which should allow spontaneous water splitting upon illumination.

Illuminated (OCP) measurements fell a few hundred mV below the hydrogen-evolution potential. Photocurrent onset measurements of V_{fb} were even further away with a mismatch of several hundred mV. Because each measurement has specific shortcomings related to material and system properties, it can be difficult to determine which V_{fb} -measurement technique provides the most believable data. Two-electrode photocurrent-potential measurements can be used to deduce which set of measurements is more reliable.

The short-circuit photocurrent density generated at zero-applied potential (in a two-electrode configuration) is interpreted commonly as representative of the amount of spontaneous water splitting occurring on the semiconductor surface. If photocurrent is observed without bias, the band-edges must be aligned (or the sample undergoing photocorrosion). The measured anodic photocurrent (Air Mass 1.5 Global Spectrum) at 0 V for $\text{In}_{0.2}\text{Ga}_{0.8}\text{N}$, $\text{In}_{0.3}\text{Ga}_{0.7}\text{N}$, and $\text{In}_{0.35}\text{Ga}_{0.65}\text{N}$ in pH 10 was found to be approximately $3.5 \mu\text{A}/\text{cm}^2$, $12 \mu\text{A}/\text{cm}^2$, and $1 \mu\text{A}/\text{cm}^2$, respectively. However, the maximum theoretical short-circuit current densities (calculated from the band-gap energies) are on the order of several mA/cm^2 . At such low current densities, it is hard to rule out photocorrosion as the source of short-circuit photocurrent. Bubbles from the electrodes can be used to infer water splitting, but bubbles were not observed for any InGaN sample, as current densities must approach $1 \text{ mA}/\text{cm}^2$ to observe bubble evolution.

FIGURE 1. Flatband potentials determined from various methods for $\text{In}_{0.3}\text{Ga}_{0.7}\text{N}$. For unbiased water splitting, the values should lie above the hydrogen half-reaction potential (solid line) for these n-type semiconductors.

We have not yet characterized the durability of these materials as these tests are terminally destructive. The durability of these InGaN samples is at the very least moderate, based on their ability to withstand the characterization techniques described above. This material set is promising based on the low band gaps, favorable band-edge positions (from M-S), and preliminary durability results. With improvements in material quality and optimization of ohmic contacts, an efficient single-junction water-splitting photoelectrode might be realized. We plan to continue studying this material class.

Thin-Film SiN System

Amorphous SiN is an attractive PEC material because it can be fabricated using scalable deposition processes that can ultimately lead to low-cost photoelectrodes. We are evaluating two sets of SiN materials: one grown by hot-wire chemical vapor deposition (HWCVD) and one grown by plasma-enhanced chemical vapor deposition (PECVD). Depending on the composition, these materials can have band-gaps that absorb visible light, making them ideal for solar energy conversion. The flatband potentials determined from open-circuit potential measurements appear to satisfy the criteria for unbiased water splitting for these intrinsically n-type semiconductors. Few single-junction semiconductor materials span the water-splitting redox potentials whereas these materials appear to do so. Two-electrode measurements demonstrate photocurrent at zero bias, which could be water splitting but is difficult to confirm because of the very low current density ($\sim \text{nanoA}/\text{cm}^2$). Even under high-reverse bias, the photocurrents observed on the HWCVD samples are limited. The relatively low photoconversion efficiencies need to be improved to achieve a viable photoelectrolysis device and could be augmented by increasing the film thickness (absorption properties) and increasing the conductivity (transport properties). We attempted to increase the HWCVD photocurrents by growing thicker films, incorporating phosphorous as an n-type dopant, using a-Si as the absorber layer, and increasing the growth temperature. None of these attempts at material optimization led to significant improvement in photocurrents.

Twenty-four hour durability tests on the HWCVD samples in 1M KOH revealed that this material is highly stable. The main degradation pathway was pinhole formation leading to delamination. The stability demonstrated by this material class is a significant result because very few semiconductor photoelectrodes exhibit corrosion resistance under extended operation. This stability could make SiN an ideal coating for photoelectrode protection if it can be sufficiently doped to facilitate current flow.

Though generating large magnitude photocurrents on HWCVD material has been unsuccessful so far, the prospect of a stable, low-cost, semiconductor that absorbs visible light and has the appropriate band-edge potentials to spontaneously split water has encouraged us to continue studying the SiN system. It is doubtful that HWCVD SiN can yield the quality materials we require for efficient photoelectrodes. Recent reports of PECVD SiN materials able to sustain several mA/cm² of photocurrent have led us to direct our attention to this new material set. PECVD is a scalable deposition technique, so this class of materials fits in line with our goal of achieving a device that can be manufactured using high-throughput techniques.

The SiN from MVSystems deposited by PECVD showed much more promising preliminary results. The bandgaps and band-edge positions are similar to the HWCVD materials. The main difference is the PECVD samples can sustain high photocurrents at a moderate bias (Figure 2). Even though SiN is intrinsically n-type, Figure 2 illustrates the response of a p-type photoelectrode, which is due to the substrate/a-SiC(p)/a-Si(i)/a-SiN(i) configuration. Two-electrode analysis of water-splitting capabilities still demonstrates low current densities, but this might be ameliorated by capping an amorphous multi-junction a-Si cell with SiN. Such a configuration might yield a durable, low-cost photoconversion device. We are currently trying to optimize this system.

FIGURE 2. Three-electrode chopped light (Air Mass 1.5 Global Spectrum) current density-potential curve showing reasonably high photocathode response on HWCVD SiN. The electrode configuration tested here is a-SiC(p)/a-Si(i)/a-SiN(i). The electrolyte was a pH₂ phosphate buffer with 10-mM Ru(NH₃)₆³⁺.

Thin-Film CGS-Based System

Thin-film CuGaSe₂ (CGS) is a material that has the potential to be a high-throughput, low-cost solar absorber. This intrinsically p-type material has a valence band edge that is too negative for the hole to drive the water oxidation half-reaction. CGS has a relatively wide bandgap (1.7 eV) and reported electrochemical stability, so it could possibly serve as the top layer of a tandem cell. Because hydrogen is evolved from the CGS surface, a hydrogen evolution catalyst would improve the gas evolution rate and enhance photoconversion efficiency. We have been studying catalysis on CGS provided by the Miller group at the Hawaii Natural Energy Institute.

The catalyst we have been focusing on is platinum with the goal of depositing nanometer-scale islands to provide facile surface reaction sites while minimizing light attenuation. One method we study is pulsed electrodeposition from chloroplatinic acid solutions where changing the pulse frequency and duty cycle can influence the catalyst morphology. The other method we employ is to physisorb platinum nanoparticles by immersing electrodes in colloidal solutions. We characterize the catalyzed electrodes with photoelectrochemical methods (chopped light current-potential) and through physical methods (scanning electron microscope, energy dispersive X-ray spectroscopy).

Synthesis and Characterization of Oxide Semiconductors

We synthesized and characterized Co-Al-Fe oxide materials based on initially promising results from Bruce Parkinson's ink-jet printed high-throughput catalyst screening system. Nanocrystalline composite electrodes were made from CoAl₂O₄ and Fe₂O₃ powders. For comparison, nanoporous CoAl₂O₄ electrodes were also prepared without adding Fe₂O₃.

The nanocomposite electrodes were prepared by mixing different amounts (5 wt% to 20 wt%) of Fe₂O₃ nanoparticles into the CoAl₂O₄ nanoparticles. The nanocomposite CoAl₂O₄-Fe₂O₃ films exhibited improved PEC response over the CoAl₂O₄ film, but the improved response (few μA/cm² under bias) was still well below what is necessary for a viable PEC device. In addition to the low magnitude of photoresponse, it took several minutes from the application of light for the response to peak. Repeated attempts to optimize these materials did not lead to improved performance. The low magnitude and slow response of the CoAl₂O₄-Fe₂O₃ films may be due to the Mott-insulator nature of these oxide materials. Mott-insulator refers to a specific electronic arrangement intrinsic to some oxides that make it almost impossible to enhance the PEC response. Due to the inherent shortcomings of this Co-Al-Fe oxide system, we reached a No-Go decision on future study of these materials.

Conclusions

- InGaN samples from LANL appear to be capable of water splitting; flatband potentials, bandgap, and durability are promising; photocurrent efficiency is below expectations for a material with this band gap.
- Hot wire chemical vapor deposited SiN has superb durability but very low photocurrents. Zero bias photocurrents may be water splitting. Repeated attempts to improve photocurrents were unsuccessful making the utility of SiN as an absorber doubtful, but it could serve as a protective coating on an amorphous multi-junction cell.
- a-SiN samples grown by MVS Systems, Inc., using plasma-enhanced chemical vapor deposition demonstrate high photocurrents under bias. Initial positive results warrant further research on this material.
- Platinum is an ideal hydrogen evolution catalyst on CGS. The optimal deposition conditions are still being investigated.
- Co-Al-Fe oxide materials are Mott-insulators, and no material optimization will yield efficient photoelectrodes; No-Go on further studies.

Future Directions

- Continue to synthesize and characterize nitride materials (GaNP, GaInPN, InGaN, SiN) for higher efficiencies and longer lifetimes in solution.
- Investigate thin-film materials (SiN, SiC, CGS) as low-cost water-splitting systems.
- Evaluate additional PEC semiconductor candidates in collaboration with others.
- Develop coatings that act as catalysts and provide corrosion protection in PEC systems.
- Develop and evaluate multi-junction structures for high efficiency.

FY 2009 Publications/Presentations

Papers

1. "Direct Water Splitting under Visible Light with Nanostructured Hematite and WO₃ Photoanodes and a GaInP₂ Photocathode," Heli Wang, Todd Deutsch, John A. Turner, *J. Electrochem Soc.*, **155**, F91 (2008).
1. "Photoelectrochemical Characterization and Durability Analysis of GaInPN Epilayers," Todd G. Deutsch, Jeff L. Head, John A. Turner, *J. Electrochem Soc.*, **155**(9), B903 (2008).
1. "ZnO Nanocoral Structures for Photoelectrochemical Cells," Kwang-Soon Ahn, Yanfa Yan, Sudhakar Shet, Kim Jones, Todd Deutsch, John Turner, Mowafak Al-Jassim, *Applied Physics Letters*, **93**, 163117 (2008).

Presentations

1. "Materials Issues for Photoelectrochemical Water Splitting, Searching for the 'Holy Grail'", Purdue University Discovery Park Hydrogen Symposium 2008 April 24, 2008 *Invited*.
2. "Solar and Hydrogen Systems: Sustainable Energy for Future Generations" 2008 Clean Energy and Power Forum, April 29, 2008 *Invited, Keynote*.
3. Frontiers, Opportunities and Challenges for a Hydrogen Economy, Sigma Xi Lecture, Naval Research Laboratory, June 13, 2008, *invited*.
4. "Frontiers, Opportunities and Challenges for a Hydrogen Economy", 10th World Renewable Energy Conference, Scotland, July 22, 2008 *Invited*.
5. "The Hydrogen Economy: Frontiers, Opportunities and Challenges", Basic Energy Sciences, Chemical Sciences Workshop on Efficient Conversion of Solar Energy to Electricity and Fuels, August 14, 2008 *Invited*.
6. "Thin-Film Nitride Semiconductors for Photoelectrolysis," 42nd Western Regional Meeting of the American Chemical Society. Las Vegas, Nevada. September 24, 2008. *Invited*
7. "Photoelectrochemical Production of Hydrogen," National Hydrogen Association Fall Forum. Golden, Colorado. September 22, 2008. *Invited*
8. "Amorphous Silicon Nitride Thin Films for Solar-Driven Photoelectrolysis," 214th Meeting of the Electrochemical Society, Joint International Meeting of the Pacific Rim Electrochemical Societies. Honolulu, Hawaii. October, 13, 2008.
9. "Optimization of Photoelectrolysis Efficiency of III-V Nitride/Silicon Tandem Semiconductor Electrodes," 214th Meeting of the Electrochemical Society, Joint International Meeting of the Pacific Rim Electrochemical Societies. Honolulu, Hawaii. October, 15, 2008.
10. "Photoelectrochemical Responses of the Nanostructured ZnO Films Synthesized using Sputtering System," 214th Meeting of the Electrochemical Society, Joint International Meeting of the Pacific Rim Electrochemical Societies. Honolulu, Hawaii. October, 15, 2008.
11. The Hydrogen Economy: Frontiers, Opportunities and Challenges, 3M Technical Forum, November 4, 2008, *Invited*.
12. Science and Technology for a Hydrogen Economy: On a Mission to Green Emission, Arizona Workshop for Renewable Energy, November 17, 2008 *Invited*.
13. The Sustainable Hydrogen Economy: Frontiers, Opportunities and Challenges, The Hydrocarbon Resources Gordon Research Conference, January 14, 2009, *Invited*.
14. Properties and Theoretical Aspects for Photoelectrochemical Water Splitting Materials, Symposium on Nanotechnology and the Environment: Emphasis on Green Nanotechnology, American Chemical Society Meeting, Salt Lake City, Utah, March 26, 2009, *Invited*.

15. Science and Technology for a Hydrogen Economy, U.S. Air Force Academy, April 6, 2009, *invited*.
16. Realizing a Sustainable Energy Future, American Physical Society Student Forum, Colorado School of Mines, May 4, 2009, *Invited*.

II.H.7 Theory of Oxides for Photo-Electrochemical Hydrogen Production

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Project Start Date: 2007
Project End Date: Project continuation and
direction determined annually by DOE

Objectives

The main focus of the project is to:

- Understand the performance of current photoelectrochemical (PEC) materials.
- Provide guidance and solution for performance improvement.
- Design and discover new materials.
- Provide theoretical basis for Go/No-Go decisions to DOE PEC H₂ projects.

Technical Barriers

This project addresses the following technical barriers from the PEC Water Splitting section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (C) Photon Absorption Coefficient
- (F) Optical and Transport Properties
- (X) Stability in Aqueous Solutions

Technical Targets

This project is intended to provide theoretical understanding of the performance of current PEC materials and provide feedback and guidance for performance improvement.

Accomplishments

- Understood the electronic properties of Fe₂O₃ and the key limiting factors for Fe₂O₃ as electrodes in PEC water splitting.
- Understood the effects of doping with transition metal on the PEC performance of Fe₂O₃.
- Understood the electronic properties of BiVO₄ and explained why BiVO₄ could be a good candidate for PEC water splitting.

Introduction

A large number of metal oxides have been under investigation for potential use as electrodes for solar PEC water splitting for hydrogen production. This project is aimed to provide theoretical understanding of the performance of current PEC materials and provide feedback and guidance for performance improvement. In this report, two materials, the Fe₂O₃ hematite, and BiVO₄ are studied theoretically. The problems associated with these materials are identified and corresponding suggestions for overcoming the problems are provided.

Hematite (α -Fe₂O₃) has long been of interest as a potential PEC material because it is among the most abundant and inexpensive semiconductors on earth with a bandgap (~2.1 eV) that is appropriate for water splitting. Hematite is stable in most electrolytes at pH > 3 and it is non-toxic. Unfortunately, pure-phase hematite is a charge transfer-type Mott insulator with intrinsically poor conductivity (by small polarons) which limits the quantum efficiency for any PEC process. To improve upon hematite's intrinsic electronic properties, substitutional doping with Si, Ti, Pt, Mo, Cr, and Ge, among other atoms, has been reported [1-5]. It is critical to understand why and how these substitutional doping could improve the hematite's electronic properties. BiVO₄ has shown particular promise for water photodecomposition with the presence of both a low band gap (2.4 – 2.5 eV) and reasonable band edge alignment with respect to the water redox potentials [6]. It has been reported to exhibit both n and p-type semiconducting properties [7], in addition to high photon-to-current conversion efficiencies. However, to date, the fundamental electronic structure of BiVO₄ has not been well explored. In particular, it is unclear whether the band gap is direct or indirect, and what role the occupied Bi 6s lone pair electrons may play in determining the valence band edge positions and charge transport. It is necessary to thoroughly understand the electronic structure of BiVO₄.

Approach

Calculations were performed using density functional theory (DFT) as implemented in the Vienna ab initio simulation package (VASP) code [8]. Three dimensional periodic boundary conditions were used to approximate an infinite solid. Gradient corrected exchange-correlation effects were described within the Perdew-Burke-Ernzerhof (PBE) functional. The core electrons were treated within the projector augmented wave (PAW) method. Both the optical transition matrix elements and optical absorption spectrum were calculated within the transversal approximation and the PAW method for BiVO_4 . For $\alpha\text{-Fe}_2\text{O}_3$, as Fe-*d* band is partially filled highly localized band, a $U = 5.5$ eV has been added to the DFT Hamiltonian. We have tested that without any U the magnetic ordering of $\alpha\text{-Fe}_2\text{O}_3$ was not correct, and the band gap was highly underestimated. With U the band gap was found to be 1.72 eV, whereas the experimental band gap is 2.2 eV. The primitive unit cell of $\alpha\text{-Fe}_2\text{O}_3$ is in rhombohedral symmetry. However, this unit cell cannot accommodate the anti-ferromagnetic (AFM) ordering as manifested by $\alpha\text{-Fe}_2\text{O}_3$. So a more conventional unit cell with 12 Fe atoms and 18 O atoms were taken as a supercell. This supercell, shown in Figure 1(a), has a layer by layer structure where each layer of Fe atoms is separated by O atoms. In addition, each layer of Fe atoms has parallel (either up or down) spin configurations, and the overall magnetic configuration is manifested here as layer-by-layer AFM. This particular magnetic configuration plays an important part in the conduction properties of this material.

Results

We first discuss why pure $\alpha\text{-Fe}_2\text{O}_3$ does not have good conductivity. Figure 1 (a) shows an Fe_2O_3 super cell, while Figure 1 (b) shows the calculated

FIGURE 1. (a) Fe_2O_3 super cell with AFM arrangements. Red and golden balls are oxygen and iron atoms, respectively. (b) Calculated band structure of Fe_2O_3 .

band structure for $\alpha\text{-Fe}_2\text{O}_3$. The main feature of the band structure is that the conduction band minima (CBM) between the *M* and *K* points in the Brillouin zone is almost completely flat, indicating extremely high electron effective mass. The lower part of the conduction band between Γ and *A* is also very flat. It implies that inter-layer conduction along *z*-direction is also highly suppressed, and is known to be four times lower than that along the layer conduction. So, electron conduction in $\alpha\text{-Fe}_2\text{O}_3$ basically takes place along the same layers where all the Fe atoms have unidirectional magnetic moment. In other words, *n*-type $\alpha\text{-Fe}_2\text{O}_3$ would not have good electron conductivity. Thus, despite the favorable band gap of around 2 eV, pure $\alpha\text{-Fe}_2\text{O}_3$ does not exhibit good PEC photo-response. On the other hand, valence band maxima lies between *M* and *K* points, has some dispersion feature. This gives holes a little less effective mass than the electrons. Site projected density of states clearly shows that the presence of highly localized Fe 3*d* band is responsible for the high electron effective mass. Because of this factor, the electron conductivity in $\alpha\text{-Fe}_2\text{O}_3$ is realized through small polaron hopping. The band structure further indicates that electron hopping between the Fe-atoms in the same layers is more probable than between the inter-layer Fe atoms.

To improve the PEC performance, $\alpha\text{-Fe}_2\text{O}_3$ has been doped with various transition metals, such as Ti, V, Cr, Ni, Pt, ... While some dopants, such as Ti, Pt, and Cr showed significant improvement in the performance, some dopants, such as Mn, showed the opposite effects. The calculated band structures for Ti doped $\alpha\text{-Fe}_2\text{O}_3$ are shown in Figure 2. Although Ti can also have 3+ oxidation states (such as in Ti_2O_3), here the substitution is not isovalent. From the spin down band structure, it is seen that the CBM is heavily modified because of the presence of Ti. The CBM are more dispersive than that of the pristine $\alpha\text{-Fe}_2\text{O}_3$. Thus, the electron

FIGURE 2. Calculated Band Structure (a) Spin Up, (b) Spin Down for Ti doped Fe_2O_3 .

effective mass of $\alpha\text{-Fe}_2\text{O}_3$ is reduced significantly after doping with Ti. The band structures further reveal that the Ti levels below CBM is partially filled indicating that Ti doped $\alpha\text{-Fe}_2\text{O}_3$ would behave as an n -type material. These results suggest that Ti doping in $\alpha\text{-Fe}_2\text{O}_3$ would significantly improve the conductivity and therefore enhance the PEC performance as observed experimentally.

We have calculated the band structures for $\alpha\text{-Fe}_2\text{O}_3$ doped with other transition metals. We found that Pt and Cr also modify the CBM of $\alpha\text{-Fe}_2\text{O}_3$, leading to more dispersive CBM and therefore reduced electron effective mass and improved electron conductivity. These explain why Pt and Cr doping would enhance the photo-response for $\alpha\text{-Fe}_2\text{O}_3$. However, doping with Mn does not change the dispersion of CBM of $\alpha\text{-Fe}_2\text{O}_3$, meaning no improvement on the electronic conductivity. In fact, Mn would create more localized defect bands leading to possible increased carrier recombination, explaining why Mn doped $\alpha\text{-Fe}_2\text{O}_3$ showed even decreased performance.

We have further proposed that Ti and N codoping may lead to even improved PEC performance. This is because Ti and N codoping leads to the following effects: 1) enhancing the doping solubility for both Ti and N; 2) increasing optical absorption in the energy region near the band gap of $\alpha\text{-Fe}_2\text{O}_3$ (2.2 eV); and 3) improving electron conductivity. Our results therefore provide suggestion for further performance improvement for $\alpha\text{-Fe}_2\text{O}_3$.

BiVO_4 (Figure 3) is a promising photocatalyst for hydrogen generation, with demonstrated experimental potential in terms of band gap, stability and conductivity. We have performed a first-principles electronic structure investigation to understand why this material is a

FIGURE 3. Representation of the crystal structure of BiVO_4 . The base centered monoclinic primitive cell is indicated by the dashed black lines.

good photocatalyst, in order to design new and better materials.

The band structure, drawn along two high symmetry lines of the Brillouin zone is shown in Figure 4. BiVO_4 is found to be a direct band gap insulator. While the PBE-DFT band gap of 2.16 eV is marginally underestimated relative to the experiment (2.4 – 2.5 eV), the difference is much less than metal oxides with s-like conduction bands such as ZnO ($\Delta E_g > 2$ eV). Quite unusually, both the valence and conduction band extrema are found away from the gamma point. While there is some curvature at the band edges, the high density of states around the band gap means that the bands are far from parabolic and are therefore not expected to be well described under a typical semiconductor effective mass approximation. However, fitting the energy-momentum dependence of the states along the A-M line predicts effective masses on the order of $0.3 m_e$ for both holes and electrons; in metal oxides typically the hole masses are much heavier, e.g. $16 m_e$ for In_2O_3 .

To gain a deeper understanding of the band structure features, we have plotted projections of the wavefunction for three specific bands at the A point through a (001) plane containing both Bi and V atoms, labeled i, ii and iii in Figure 4. The first projection at -9.1 eV is of predominately Bi 6s character (as expected from the corresponding DOS in this energy range); significant hybridization between Bi and the neighboring

FIGURE 4. Calculated electronic band structure along the Γ -A-M lines. The highest occupied state is set to 0 eV. Charge density contour plots are shown for three bands at the A point (plotted from 0 to $0.01 \text{ e} \cdot \text{\AA}^{-3}$).

O can also be observed. The second projection at 0 eV is dominated by Bi and O character. Here the density node between Bi and O is suggestive of the antibonding nature of their interaction. Due to the role of symmetry and orbital phase constraints, Bi s – O p coupling does not occur at the gamma point, which results in the upwards dispersion towards A, where this interaction is maximized. The final projection is of the conduction band minimum states, which contains contributions from V d, O p and Bi p. The resulting energy level interactions are summarized in Figure 4. At gamma, the valence and conduction band extrema contain contributions solely from O 2p and V 3d, respectively. Away from the zone centre, coupling with Bi s (valence band) and Bi p/O p (conduction band) is observed. Quantitatively, the Bi s – O p interaction results in a 0.4 eV energy raise in the valence band maxima.

Conclusions and Future Directions

We have calculated the electronic structure of α -Fe₂O₃ and BiVO₄, using DFT. We have provided detailed understanding on why pure α -Fe₂O₃ would not exhibit very good PEC response, and why doping with some transition elements would lead to improved performance, but doping with other transition metals lead to decreased performance. We proposed a method on how to further improve the PEC performance for α -Fe₂O₃. For BiVO₄, we found that BiVO₄ is a direct band gap semiconductor, despite having band extrema away from the Brillouin zone center. Coupling between Bi 6s and O 2p forces an upward dispersion of the valence band at the zone boundary; however, a direct gap is maintained via coupling between V 3d, O 2p and Bi 6p, which lowers the conduction band minimum. These interactions result in symmetric hole and electron masses. Implications for the design of ambipolar metal oxides are discussed.

Future Directions

- Extend our research to other metal oxides.
- Design new metal oxides with desirable optical absorption, band edge positions, and transport properties.
- Extend our study to non-oxide materials, such as nitrides, carbides, sulfides, ...

FY 2009 Publications/Presentations

1. M.N. Huda, Yanfa Yan, C.-Y. Moon, S.-H. Wei, and M.M. Al-Jassim, "Density-functional theory study of the effects of atomic impurity on the band edges of monoclinic WO₃," *Phys. Rev B* **77**, 195102 (2008).
2. Aron Walsh, Yanfa Yan, M.M. Al-Jassim, and S.-H. Wei, "Electronic, Energetic, and Chemical Effects of Intrinsic Defects and Fe-Doping of CoAl₂O₄: A DFT+U Study," *J. Phys. Chem. C* **112**, 12044 (2008).
3. M.N. Huda, Yanfa Yan, S.-H. Wei, and M.M. Al-Jassim, "Electronic structure of ZnO:GaN compounds: Asymmetric bandgap engineering," *Phys. Rev. B* **78**, 195204 (2008).
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5. M.N. Huda, Yanfa Yan, S.-H. Wei, and M.M. Al-Jassim, "An Electronic Structure Study of Intermediate Band by Non-Magnetic Ion Doping in WO₃," 2008 MRS Fall Meeting, Boston
6. Yanfa Yan, A. Walsh, M.N. Huda, S.H. Wei, M.M. Al-Jassim, Y.S. Hu, E. McFarland, "Understanding the PEC performance of Fe₂O₃," DOE PEC H₂ working group meeting, Hawaii, 2008

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II.H.8 Photoelectrochemical Hydrogen Production: MVSystems Incorporated

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Contract Number: DE-FG36-07GO17105

Subcontractor:

University of Hawaii at Manoa (UH), Honolulu, HI

Project Partner:

National Renewable Energy Laboratory (NREL),
Golden, CO

Project Start Date: November 1, 2007

Project End Date: August 31, 2009

Objectives

- Work closely with the DOE Working Group on photoelectrochemical (PEC) hydrogen production to develop and employ new theoretical, synthesis and analytical techniques for optimizing PEC materials and devices.
- Develop new PEC film materials compatible with high-efficiency, low-cost hydrogen production devices based on amorphous-silicon-compound, tungsten-compound and copper-chalcopyrite compound classes of thin films.
- Demonstrate functional multi-junction device incorporating best-available PEC film materials developed.
- Explore avenues toward manufacture-scaled devices and systems.

Technical Barriers

This project addresses the following technical barriers from the "Photoelectrochemical Hydrogen Production" section of the Hydrogen, Fuel Cells

and Infrastructure Technologies Program Multi-year Research, Development and Demonstration Plan:

- (Y) Materials Efficiency
- (Z) Materials Durability
- (AA) PEC Device and System Auxiliary Material
- (AB) Bulk Materials Synthesis
- (AC) Device Configuration Designs

Technical Targets

The specific targets of this project are (a) the demonstration of a PEC solar-hydrogen production system with 7.5% solar-to-hydrogen (STH) conversion efficiency (b) operational life up to 500 hours and (c) the identification of commercialization paths toward a \$22/kg-H₂ plant production cost by 2010 and \$5/kg by 2015. Table 1 shows detailed milestones year by year.

TABLE 1. DOE Targets for Photoelectrochemical Hydrogen Production

Task #	Milestone	Note
Year 1	Material photocurrent ≥ 3 mA/cm ²	Achieved
	Durability ≥ 100 hr	Achieved
Year 2	Material photocurrent ≥ 4 mA/cm ²	Achieved
	Durability ≥ 200 hr	
	Device STH efficiency $\geq 5\%$	
GO/NO-GO Decision Evaluated		
Year 3	Device STH efficiency $\geq 6.15\%$ over 300 hours	
Year 4	Device STH efficiency $\geq 7.5\%$ over 500 hours	

Accomplishments

- New approaches in tungsten oxide surface treatment:
 - Photocurrent above 3.5 mA/cm² (at 1.6 V vs. saturated calomel electrode) demonstrated with molybdenum incorporation in WO₃ near surface (approximately 300 nm) to form a bilayer.
 - Evaluation of RuO₂ as catalyst for oxygen evolution reaction. Enhancement of devices performances demonstrated with both RuO₂ thin film and nanoparticles.
- New Cu(In,Ga)(S,Se) alloys have matched previously reported photocurrents (~ 20 mA/cm²) while reducing required voltage bias by ~ 200 mV.
- Successfully fabricated the hybrid photovoltaic (PV)/a-SiC device consisting of amorphous silicon

(a-Si) tandem solar cell and amorphous silicon carbide (a-SiC) photoelectrode, which exhibits the following PEC performance:

- Flat-band potential in a pH2 electrolyte (determined by the illuminated open-circuit potential) is +1.88 V relative to Ag/AgCl reference electrode, or +0.97 V below the $\text{H}_2\text{O}/\text{O}_2$ redox potential and is in an appropriate position to facilitate water splitting.
- Photocurrent is 4-5 mA/cm^2 measured in 3-electrode setup; $\sim 1 \text{ mA}/\text{cm}^2$ at zero bias using 2-electrode setup. Hydrogen production has been observed.
- Good durability in pH2 buffered electrolyte for up to 150 hours (test is on-going).

Introduction

Based on its potential to meet long-term goals, research and development (R&D) centering on multijunction hybrid photoelectrode technology defines the scope of this collaborative project. Within this scope, particular emphasis is placed on the most critical materials-research components in terms of efficiency, durability and cost. To achieve 7.5% STH conversion efficiency and up to 500-hour operational life along with production cost goals, the development of low-cost photoactive materials with photocurrents $>6 \text{ mA}/\text{cm}^2$ and with sufficient durability to meet the lifetime requirement will be the key focus. Development of specific thin-film materials classes with promising PEC potential, including tungsten-based compounds (such as metal and mixed-metal oxides, oxy-nitrides, oxy-sulfides, etc.), copper-chalcopyrite compounds (including CIGSe_2 , CGSe_2 , etc.) and silicon-based compounds (such as silicon carbide and silicon nitride) is the specific focus of this R&D project. In addition to the materials R&D activities, development of laboratory-scale demonstration devices and generation of preliminary commercialization studies is included in the project scope as second-level priorities. To support the device-demonstration activities, appropriate auxiliary components have been developed for incorporation in the PEC photoelectrode designs (i.e., the hybrid PV/a-SiC PEC cells). It is the central objective of the MVSystems project team to work closely with the DOE Working Group on PEC Hydrogen Production to develop pathways for successful PEC hydrogen technologies.

Approach

The general approach of this collaborative effort focuses on the DOE PEC Working Group's "feedback" philosophy integrating state-of-the-art theoretical, synthesis and analytical techniques to identify and develop the most promising materials classes to meet

the PEC challenges in efficiency, stability and cost.

Materials modeling, bulk-film optimization, film-surface enhancement, along with comprehensive material and device characterization is being employed to facilitate the R&D process. Specifically, the feedback approach is being applied to our focus material classes, including the tungsten-, copper-chalcopyrite- and silicon-based compounds, to enhance understanding of fundamental performance parameters, and expedite development of process-compatible forms of these materials. The primary objective of the materials research efforts is the development of films which meet photocurrent and durability goals and which are compatible with device fabrication. The most promising candidate materials will be identified, with the short-term goal of demonstrating laboratory-scale water-splitting devices, and with a long-term goal of transferring the fabrication processes toward the commercial scale.

Results

During this reporting period, extensive studies of the three materials classes under investigation have focused on understanding and improving photoelectrochemical behavior, specifically by applying our theoretical, synthesis and analytical techniques in identifying relevant aspects of structural, optoelectronic and electrochemical properties. Progress in developing each of the focus materials is detailed in the following subsections.

Tungsten-Based Compound Films

Several experiments on tungsten oxide surface modifications have been initiated during this period. A WO_3 surface modification using molybdenum (referred as $\text{WO}_3:\text{Mo}$) was fabricated using a reactive co-sputtering process. Molybdenum incorporation was performed at the end of the WO_3 film synthesis to form a $\text{WO}_3:\text{Mo}(300 \text{ nm})/\text{WO}_3(2 \text{ }\mu\text{m})$ bilayer. PEC tests performed under simulated AM1.5 illumination in 0.33M H_3PO_4 pointed out a saturated photocurrent increase of approx. 20% at 1.6 V vs. SCE with the bilayer PEC electrode ($3.6 \text{ mA}/\text{cm}^2$) when compared to pure WO_3 materials ($2.9 \text{ mA}/\text{cm}^2$). Subsequent surface analyses performed at the University of Nevada, Las Vegas (UNLV) revealed a WO_3 work function increase of approximately 0.2 eV after Mo incorporation. The difference in the Fermi level positions between the two materials would create a built-in potential at the $\text{WO}_3:\text{Mo}/\text{WO}_3$ interface that could enhance hole transfer to the electrolyte.

Surface modification with RuO_2 nanoparticles to increase catalytic activity on WO_3 was also investigated. First, a series of experiments were conducted on RuO_2 thin films to establish a baseline deposition process. Catalytic activity for the oxygen evolution reaction was

validated using RuO_2 thin film as a counter electrode for a p-type PEC electrode test. Onset potential reductions of about 400 mV were observed for both a-SiC and CGSe-based PEC electrodes. Nanoparticles were then deposited on several substrates using the same process with a 30-second deposition time. High catalytic activity was observed with RuO_2 nanoparticles deposited on conductive transparent oxide ($\text{SnO}_2\text{:F}$) substrates. Figure 1 presents a scanning electron microscope micrograph of the nanoparticles deposited on WO_3 .

Copper Chalcopyrite-Based Films

Progress in PEC water-splitting using copper chalcopyrite thin-films has identified specific avenues of future work required to reach the DOE targets for PEC hydrogen production. Copper gallium diselenide (CGSe) thin-films exhibit extremely high photocurrents ($\sim 20 \text{ mA/cm}^2$) under 1-sun AM1.5G illumination in 0.5M sulfuric acid with a very high degree of durability. This class of materials requires a high voltage bias to initiate the water-splitting reaction. The deposition process of baseline CGSe thin films is robust and reproducible, and optimization of the films for high photocurrents is well beyond what is needed to reach the DOE Targets. We will shift our focus to decrease the voltage bias which is caused by a valence band mismatch with the half-reaction potential for the oxygen evolution reaction.

Variations of the copper chalcopyrite material alloy class ($\text{Cu}(\text{In}_x\text{Ga}_{1-x})(\text{S}_y\text{Se}_{1-y})_2$) (CIGS) allows the tuning of the material bandgap. Experimentation has further shown that the partial or full replacement of selenium

FIGURE 1. Scanning electron microscopy micrograph of WO_3 film treated with RuO_2 nanoparticles. The resulting 3-5 nm particles cover approximately 35% of the total area.

with sulfur can modify the band edges as well. Samples of CIGS (with sulfur completely replacing selenium) provided by Bjorn Marsen at the Helmholtz Zentrum Berlin matched the photocurrent of champion CGSe films ($\sim 20 \text{ mA/cm}^2$) while reducing the required voltage bias by nearly 200 mV, a marked improvement. Further material characterization is needed to fully understand these new materials.

Amorphous Silicon Carbide-Based Compound Films

During this project period, significant progress has been made in the study of a-SiC photoelectrodes used in water splitting for hydrogen production. We have successfully integrated the a-SiC photoelectrode with a-Si tandem solar cell to form a hybrid PEC cell. Figure 2 shows the configuration used for the hybrid PEC device, consisting of an a-Si:H tandem solar cell (thickness of the top and bottom cell is 80 nm and 360 nm respectively) and a-SiC:H photoelectrode which contains an intrinsic a-SiC ($\sim 100 \text{ nm}$ thick) and a thin p-type a-SiC:B layer ($\sim 10 \text{ nm}$ thick). The substrate used for the hybrid PEC device was typically fluorine doped tin oxide (Asahi U- type) coated glass. Other types of substrates such stainless steel (SS) and zinc oxide (ZnO) coated glass were also used for comparison purposes. The a-Si:H tandem solar cell which was used in the hybrid PEC device exhibited V_{oc} (open-circuit voltage) = 1.66 V, J_{sc} (short-circuit current density) = 8.7 mA/cm^2 , fill factor (FF) = 0.67, and efficiency of $\sim 9.6\%$. The flat-band potential of the hybrid PEC cell in a pH2 electrolyte, as determined by the illuminated open-circuit potential method, shifts significantly from +0.26 V (vs. Ag/AgCl) to +0.97 V below the $\text{H}_2\text{O/O}_2$ half-reaction potential and is in an appropriate position to facilitate water splitting. Figure 3 shows the current density vs. potential characteristics for hybrid PEC device fabricated on different substrates, including SnO_2 and ZnO coated glass as well as SS, and measured in the pH2 buffered electrolyte (sulphamic acid solution with added potassium biphthalate) using the 3-electrode. We

FIGURE 2. Configuration of the Hybrid PEC Device

FIGURE 3. Current Density vs. Potential Characteristics of the PV/a-SiC PEC Devices.

see that the saturated photocurrent of the hybrid cell using different substrates is in the range of 3-5 mA/cm², potentially leading to a STH efficiency of ~5.5%. The larger photocurrent on SnO₂ (>4 mA/cm²) coated glass substrate is due to the inherent texture of the SnO₂ which enhances internal photon absorption.

The photocurrent density at a zero potential reaches ~1 mA/cm² measured using the 2-electrode setup (not shown here). Hydrogen production was observed in short-circuit condition, as shown in Figure 4(a). It should be noted that compared with the 3-electrode case, the photocurrent measured in the 2-electrode setup is much lower, suggesting limiting factors. We have noted that the over-potential loss in the 2-electrode setup can be due to, (1) type of electrolyte used, (2) type of counter electrode used and (3) formation of thin SiOx layer on the a-SiC surface. Initial results have shown that, after dipping the hybrid device into 5% hydrofluoric acid for 30 seconds and using RuO₂ as the counter electrode, the photocurrent is enhanced from 0.33 to 0.83 mA/cm² at zero bias.

The hybrid PEC cell exhibits good durability in the pH2 buffered electrolyte for up to 148 hours (so far performed). The dark current shows almost no change, and hence no corrosion occurring on the hybrid device after the 148-hr test, as is evident also in Figure 4(b).

Conclusions and Future Directions

The MVSystems/UH project is accelerating the development of three important PEC thin-film materials classes (a-SiC, WO₃ and CGSe) with high potential for reaching DOE goals of practical PEC water-splitting. The project benefits from existing knowledge of the three PEC thin-film materials and their PV performances. This knowledge can be applied to a PEC system for hydrogen production. For each material, barriers were identified and major improvements are currently being made to improve PEC performances. New surface modification techniques were investigated, including

FIGURE 4. (a) Demonstration of hydrogen evolution in the hybrid PEC device, measured in the short-circuit condition. (b) Photo images of the hybrid PEC device prior to and after a 148-hr test in pH2 electrolyte.

oxide etch (a-SiC), bilayer formation and nanoparticles deposition (WO₃). Bulk modifications were investigated, such as CIGSe film sulfurization to modify energy band position. Resulting interface and bulk energy band positions will be characterized using UNLV advanced spectroscopic techniques. This new information will guide our research on device fabrication and device matching efforts effectively.

FY 2009 Publications/Presentations

1. F. Zhu, J. Hu, I. Matulionis, T. Deutsch, N. Gaillard, A. Kunrath, E. Miller, A. Madan, *Amorphous silicon carbide photoelectrode for hydrogen production directly from water using sunlight*, Phil. Mag. B85, (2009) 1-16.
2. J. Hu, I. Matulionis, F. Zhu, J. Gallon, T. Deutsch, N. Gaillard, A. Kunrath, E. Miller, and A. Madan, Development of a photovoltaic (PV)/photoelectrochemical (PEC) hybrid device with amorphous silicon carbide as the photoelectrode for water splitting, MRS spring meeting, San Francisco, 2009.
3. F. Zhu, J. Hu, I. Matulionis, A. Kunrath, and A. Madan, *Properties of Nano-crystalline Silicon-Carbide Films Prepared Pulse Using Modulated RF-PECVD*, MRS spring meeting, San Francisco, 2009.
4. Y. Zhang, K. George, M. Bär, C. Heske, J. Hu, F. Zhu, and A. Madan, *Chemical and electronic structure of SiC thin films for photoelectrochemical water splitting*, MRS spring meeting, San Francisco, 2009.

5. N. Gaillard, J. Kaneshiro, E.L. Miller, L. Weinhardt, M. Bär, C. Heske, K.-S. Ahn, Y. Yan, and M.M. Al-Jassim, *Surface Modification of Tungsten Oxide-Based Photoanodes for Solar-Powered Hydrogen Production*, MRS spring meeting, San Francisco, 2009.
6. N. Gaillard, B. Cole, B. Marsen, J. Kaneshiro, E.L. Miller, L. Weinhardt, M. Bär, C. Heske, K.-S. Ahn, Y. Yan, and M.M. Al-Jassim, *Improved current collection in WO_3 :Mo/ WO_3 bilayer photoelectrodes*, to be published in Journal of Material Research.
7. J. Kaneshiro, E. Miller, N. Gaillard and R. Rocheleau, *Advances in Copper Chalcopyrite Thin Films for Solar Energy Conversion*, to be published in Sol. Energy Mater. and Sol. Cells.

II.H.9 Progress in the Study of Amorphous Silicon Carbide (a-SiC) as a Photoelectrode in Photoelectrochemical (PEC) Cells

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Contract Number: DE-FG36-07GO17105

Project Partner:

National Renewable Energy Laboratory (NREL),
Golden, CO

Project Start Date: November 1, 2007
Project End Date: August 31, 2009

Objectives

- Work closely with the DOE Working Group on PEC Hydrogen Production to develop and employ new theoretical, synthesis and analytical techniques for optimizing PEC materials and devices.
- Develop new PEC film materials compatible with high-efficiency, low-cost hydrogen production devices based on amorphous-silicon-compound, tungsten-compound and copper-chalcopyrite compound classes of thin films.
- Demonstrate functional multi-junction device incorporating best-available PEC film materials developed.
- Explore avenues toward manufacture-scaled devices and systems.

Technical Barriers

This project addresses the following technical barriers from the “Photoelectrochemical Hydrogen Production” section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-year Research, Development and Demonstration Plan:

(Y) Materials Efficiency

(Z) Materials Durability

(AA) PEC Device and System Auxiliary Material

(AB) Bulk Materials Synthesis

(AC) Device Configuration Designs

Technical Targets

The specific targets of this project are (a) the demonstration of a PEC solar-hydrogen production system with 7.5% solar-to-hydrogen (STH) conversion efficiency (b) operational life up to 500 hours and (c) the identification of commercialization paths toward a \$22/kg-H₂ plant production cost. Table 1 shows detailed milestones year by year.

TABLE 1. DOE Targets for Photoelectrochemical Hydrogen Production

Task #	Milestone	Note
Year 1	Material photocurrent ≥ 3 mA/cm ²	Achieved
	Durability ≥ 100 hr	Achieved
Year 2	Material photocurrent ≥ 4 mA/cm ²	Achieved
	Durability ≥ 200 hr	
	Device STH efficiency $\geq 5\%$	
GO/NO-GO decision evaluated		
Year 3	Device STH efficiency $\geq 6.15\%$ over 300 hours	
Year 4	Device STH efficiency $\geq 7.5\%$ over 500 hours	

Accomplishments

New Approaches in Tungsten Oxide Surface Treatment:

- Photocurrent above 3.5 mA/cm² (at 1.6 V vs. saturated calomel electrode, SCE) demonstrated with molybdenum incorporation in WO₃ near surface (approximately 300 nm) to form a bilayer.
- Evaluation of RuO₂ as catalyst for oxygen evolution reaction. Enhancement of devices performances demonstrated with both RuO₂ thin film and nanoparticles.

Introduction

Based on its potential to meet long-term goals, research and development (R&D) centering on multijunction hybrid photoelectrode technology defines the scope of this collaborative project. Within this

scope, particular emphasis is placed on the most critical materials-research components in terms of efficiency, durability and cost. To achieve 7.5% STH conversion efficiency and up to 500-hour operational life along with production cost goals, the development of low-cost photoactive materials with photocurrents $>6 \text{ mA/cm}^2$ and with sufficient durability to meet the lifetime requirement will be the key focus. Development of specific thin-film materials classes with promising PEC potential, including tungsten-based compounds (such as metal and mixed-metal oxides, oxy-nitrides, oxy-sulfides, etc.), copper-chalcopyrite compounds (including CuInSe_2 , CuGeSe_2 , etc.) and silicon-based compounds (such as silicon carbide and silicon nitride) is the specific focus of this R&D project. In addition to the materials R&D activities, development of laboratory-scale demonstration devices and generation of preliminary commercialization studies is also included in the project scope as second-level priorities. To support the device-demonstration activities, appropriate auxiliary components have been also in development for incorporation in the PEC photoelectrode designs (i.e., the hybrid photovoltaic [PV]/a-SiC PEC cells). It is the central objective of the MVSsystems project team to work closely with the DOE Working Group on PEC Hydrogen Production to develop pathways for successful PEC hydrogen technologies.

Approach

The general approach of this collaborative effort focuses on the DOE PEC Working Group's "feedback" philosophy integrating state-of-the-art theoretical, synthesis and analytical techniques to identify and develop the most promising material classes to meet the PEC challenges in efficiency, stability and cost. Materials modeling, bulk-film optimization, film-surface enhancement, along with comprehensive material and device characterization is being employed to facilitate the R&D process. Specifically, the feedback approach is being applied to our focus material classes, including the tungsten-, copper-chalcopyrite- and silicon-based compounds, to enhance understanding of fundamental performance parameters, and expedite development of process-compatible forms of these materials. The primary objective of the materials research efforts is the development of films which meet photocurrent and durability goals and which are compatible with device fabrication. The most promising candidate materials will be identified, with the short-term goal of demonstrating laboratory-scale water-splitting devices, and with a long-term goal of transferring the fabrication processes toward the commercial scale.

Results

During this reporting period of the project (June 2008 – June 2009), extensive studies of the three

materials classes under investigation have focused on understanding and improving PEC behavior, specifically by applying our theoretical, synthesis and analytical techniques in identifying relevant aspects of structural, optoelectronic and electrochemical properties. Specific progress in developing the tungsten-based materials is detailed in the following subsections.

Tungsten-Based Compound Films

Several experiments on tungsten oxide surface modifications have been initiated during this period. A WO_3 surface modification using molybdenum (referred as $\text{WO}_3:\text{Mo}$) was fabricated using a reactive co-sputtering process. Molybdenum incorporation was performed at the end of the WO_3 film synthesis to form a $\text{WO}_3:\text{Mo}$ (300 nm)/ WO_3 (2 μm) bilayer. Photoelectrochemical tests performed under simulated AM1.5 illumination in 0.33 M H_3PO_4 pointed out a saturated photocurrent increase of approx. 20% at 1.6 V vs. SCE with the bilayer PEC electrode (3.6 mA/cm^2) when compared to pure WO_3 materials (2.9 mA/cm^2), as presented in Figure 1. Subsequent surface analyses performed at the University of Nevada, Las Vegas (UNLV) revealed a WO_3 work function increase of approx. 0.2 eV after Mo incorporation. The difference in the Fermi level positions between the two materials would create a built-in potential at the $\text{WO}_3:\text{Mo}/\text{WO}_3$ interface that could enhance hole transfer to the electrolyte.

Surface modification with RuO_2 nanoparticles to increase catalytic activity on WO_3 was also investigated. First, a series of experiments were conducted on RuO_2 thin films to establish a baseline deposition process.

FIGURE 1. Current-potential characteristics measured for WO_3 (open circles), $\text{WO}_3:\text{Mo}$ (open squares), and $\text{WO}_3:\text{Mo}/\text{WO}_3$ bi-layer (open triangles) PEC electrodes in 0.33M H_3PO_4 under chopped simulated AM1.5G illumination (scan rate: 25 mV/s).

FIGURE 2. Current vs. potential curves measured in 0.33 M H₃PO₄ electrolyte on TEC15 substrate before (green curve) and after a 15 second (blue curve) or 30 second (red curve) RuO₂ nanoparticles deposition.

Catalytic activity for the oxygen evolution reaction was validated using RuO₂ thin film as a counter electrode for a p-type PEC electrode test. Onset potential reductions of about 400 mV were observed for both a-SiC and CGSe-based PEC electrodes. Nanoparticles were then deposited on TEC15 substrates using the same process with a 15 or 30-second long deposition time. High catalytic activity of RuO₂ nanoparticles was observed, with a reduction of the oxygen evolution reaction onset potential of more than 1 V (see Figure 2). More important, the effect of deposition time (i.e. the size of the particles) has a negligible effect on the onset potential. This important discovery will be crucial to maximize light harvesting of tungsten oxide film treated with nanoparticles. In fact, a 30 second RuO₂ deposition process covers 35% of the WO₃ surface with 5 nm particles, as presented in Figure 3.

Conclusions and Future Directions

The MVSystems/UH project is accelerating the development of three important PEC thin-film materials classes (a-SiC, WO₃ and CGSe) with high potential for reaching DOE goals of practical PEC water-splitting. The project benefits from existing knowledge of the three PEC thin-film materials and their PV performances to apply them to a PEC system for hydrogen production. For each material, barriers were identified and major improvements are currently being made to improve PEC performances. New surface modification techniques were investigated, including oxide etch (a-SiC), bilayer formation and nanoparticles deposition (WO₃). Bulk

FIGURE 3. Scanning electron microscopy micrograph of WO₃ film treated with RuO₂ nanoparticles. The resulting 3-5 nm particles cover approximately 35% of the total area.

modifications were also investigated, such as CIGSe film sulfurization to modify energy band position. Resulting interface and bulk energy band positions will be characterized using UNLV advanced spectroscopic techniques. These new information will guide our research on device fabrication and device matching efforts effectively.

FY 2009 Publications/Presentations

1. F. Zhu, J. Hu, I. Matulionis, T. Deutsch, N. Gaillard, A. Kunrath, E. Miller, A. Madan, *Amorphous silicon carbide photoelectrode for hydrogen production directly from water using sunlight*, Phil. Mag. B85, (2009) 1-16.
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4. Y. Zhang, K. George, M. Bär, C. Heske, J. Hu, F. Zhu, and A. Madan, *Chemical and electronic structure of SiC thin films for photoelectrochemical water splitting*, MRS spring meeting, San Francisco, 2009.
5. N. Gaillard, J. Kaneshiro, E.L. Miller, L. Weinhardt, M. Bär, C. Heske, K.-S. Ahn, Y. Yan, and M.M. Al-Jassim, *Surface Modification of Tungsten Oxide-Based Photoanodes for Solar-Powered Hydrogen Production*, MRS spring meeting, San Francisco, 2009.

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7. J. Kaneshiro, E. Miller, N. Gaillard and R. Rocheleau, *Advances in Copper Chalcopyrite Thin Films for Solar Energy Conversion*, to be published in Sol. Energy Mater. and Sol. Cells.

II.H.10 Progress in the Study of Copper Chalcopyrites as Photoelectrodes in Photoelectrochemical Cells

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Contract Number: DE-FG36-07GO17105

Project Partner:
National Renewable Energy Laboratory (NREL),
Golden, CO

Project Start Date: November 1, 2007
Project End Date: August 31, 2009

Objectives

- Work closely with the DOE Working Group on Photoelectrochemical (PEC) Hydrogen Production to develop and employ new theoretical, synthesis and analytical techniques for optimizing PEC materials and devices.
- Develop new PEC film materials compatible with high-efficiency, low-cost hydrogen production devices based on amorphous-silicon-compound, tungsten-compound and copper-chalcopyrite compound classes of thin films.
- Demonstrate functional multi-junction device incorporating best-available PEC film materials developed.
- Explore avenues toward manufacture-scaled devices and systems.

Technical Barriers

This project addresses the following technical barriers from the "Photoelectrochemical Hydrogen Production" section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year

Research, Development and Demonstration (Multi-Year RD&D) Plan:

- (Y) Materials Efficiency
- (Z) Materials Durability
- (AA) PEC Device and System Auxiliary Material
- (AB) Bulk Materials Synthesis
- (AC) Device Configuration Designs

Technical Targets

As recognized within the PEC hydrogen research community and the DOE Hydrogen Program, the technology is still far from maturity, and the most critical technical issues relate to the development of suitable photoactive semiconductors for water-splitting. Of the four DOE technical characteristics outlined in the Multi-Year RD&D Plan for PEC hydrogen production (see Table 1), targets in the first category ("useable semiconductor band gap") are the primary focus of research, with secondary emphasis on the second category targets ("chemical conversion process efficiency").

TABLE 1. DOE Targets for Photoelectrochemical Hydrogen Production

Characteristic	Units	2006 Status	2013 Target	2018 Target
Useable Semiconductor Band Gap	eV	2.8	2.3	2.0
Chemical Conversion Process Efficiency (EC)	%	4	10	12
Plant STH Efficiency	%	N/A	8	10
Plant Durability	hrs	N/A	1,000	5,000

STH – solar to hydrogen; N/A - not applicable

The specific targets of this project are the demonstration of a PEC solar-hydrogen production system with 7.5% STH conversion efficiency and operational life up to 500 hours; and the identification of commercialization paths toward a \$22/kg-H₂ plant production cost.

Accomplishments

- Robust deposition recipe consistently producing cells with 16-20 mA/cm² saturated photocurrent.
- New Cu(In,Ga)(S,Se) alloys have matched previously champion photocurrents (~20 mA/cm²) while reducing required voltage bias by ~200 mV with the complete replacement of Se with S.
- Very high degree of stability demonstrated in new materials.
- Identifying avenues of improvement.

Introduction

Based on its potential to meet long-term goals, research and development (R&D) centering on multijunction hybrid photoelectrode technology defines the scope of this collaborative project. Within this scope, particular emphasis will be put on the most critical materials-research components in terms of efficiency, durability and cost. To achieve 7.5% STH conversion efficiency and up to 500-hour operational life along with production cost goals, the development of low-cost photoactive materials with photocurrents greater than 6 mA/cm² and with sufficient durability to meet the lifetime requirement will be the key focus. Development of specific thin-film materials classes with promising PEC potential, including tungsten-based compounds (such as metal and mixed-metal oxides, oxy-nitrides, oxy-sulfides, etc.), copper-chalcopyrite compounds (including CIGSe₂, CGSe₂, etc.) and silicon-based compounds (such as silicon carbide and silicon nitride) is the specific focus of this R&D effort. In addition to the materials R&D activities, development of laboratory-scale demonstration devices and generation of preliminary commercialization studies is also included in the project scope as second-level priorities. To support the device-demonstration activities, appropriate auxiliary components have been also in development for incorporation in PEC photoelectrode designs (i.e., the hybrid photovoltaic [PV]/a-SiC PEC cells). It is the central objective of the MVSystems project team to work closely with the DOE Working Group on PEC Hydrogen Production to develop pathways for successful PEC hydrogen technologies.

Approach

The general approach of this collaborative effort focuses on the DOE PEC Working Group's "feedback" philosophy integrating state-of-the-art theoretical, synthesis and analytical techniques to identify and develop the most promising materials classes to meet the PEC challenges in efficiency, stability and cost. Materials modeling, bulk-film optimization, film-surface

enhancement, along with comprehensive material and device characterization is being employed to facilitate the R&D process. Specifically, the feedback approach is being applied to our focus material classes, including the tungsten-, copper-chalcopyrite- and silicon-based compounds, to enhance understanding of fundamental performance parameters, and expedite development of process-compatible forms of these materials. The primary objective of the materials research efforts is the development of films which meet photocurrent and durability goals, and which are compatible with device fabrication. The most promising candidate materials will be identified, with the short-term goal of demonstrating laboratory-scale water-splitting devices, and with a long-term goal of transferring the fabrication processes toward the commercial scale.

Results

During this reporting period of the project (June 2008 – June 2009), extensive studies of the three material classes under investigation have focused on understanding and improving photoelectrochemical behavior, specifically by applying our theoretical, synthesis and analytical techniques in identifying relevant aspects of structural, optoelectronic and electrochemical properties. Specific progress in developing the copper chalcopyrite materials class is detailed in the following subsections.

Copper Chalcopyrite-Based Films

Progress in PEC water-splitting using copper chalcopyrite thin-films has identified specific avenues of future work required to reach the DOE Targets for Photoelectrochemical Hydrogen Production.

Copper gallium diselenide (CGSe) thin-films exhibit extremely high photocurrents (~20 mA/cm²) under 1-sun AM1.5G illumination in 0.5 M sulfuric acid with a very high degree of durability. This class of materials suffers, however, from a high required voltage bias to initiate the water-splitting reaction resulting from a high valence band maximum (VBM) in relation to the oxygen evolution energy.

The deposition process of baseline CGSe thin films is robust and reproducible, and optimization of the films for high photocurrents is well beyond what is needed to reach the DOE targets. Focus has shifted, therefore, to the reduction of the high required voltage bias. Partial platinization of the surface has begun to show some improvement in the required voltage bias, warranting further experimentation with surface treatments.

Alloy variations of the copper chalcopyrite material class (Cu(In_xGa_(1-x))(S_ySe_(1-y))₂) have already been shown to allow tuning of the material bandgap. It has been theorized and experimentation has begun to show that

the partial or full replacement of selenium with sulfur can modify the band edge positions themselves. As seen in Figure 1, samples of copper indium gallium diselenide (CIGS) compounds (with sulfur completely replacing selenium) provided by Bjorn Marsen at the Helmholtz Zentrum Berlin matched the photocurrent of champion CGSe films ($\sim 20 \text{ mA/cm}^2$) while reducing the required voltage bias by nearly 200 mV, a marked improvement. Further material characterization is needed to fully understand these new materials.

It has also been suggested that the partial or full replacement of In and/or Ga with Al could also lower the VBM. Unfortunately, aluminum selenide is unstable in water and air and decomposes to form highly toxic gases, precluding its use anywhere in CIGSe systems and films. The complete replacement of selenium with sulfur, however, may permit the inclusion of aluminum. Another possible avenue to lower the VBM is to partially or fully replace Cu with Ag. While it would make films more expensive, these thin-film cells use a very small amount of source material.

Conclusions and Future Directions

The MVSystems/UH project is accelerating the development of three important PEC thin-film materials classes (a-SiC, WO_3 and CGSe) with high potential for reaching DOE goals of practical PEC water-splitting. The project benefits from existing knowledge of the three PEC thin-film materials and their PV performance to application to a PEC system for hydrogen production. For each material, barriers were identified and major improvements are currently being made to improve PEC

performance. New surface modification techniques were investigated, including oxide etch (a-SiC), bilayer formation and nanoparticles deposition (WO_3). Bulk modifications were also investigated, such as CIGSe film sulfurization to modify energy band position. Resulting interface and bulk energy band positions will be characterized using University of Nevada, Las Vegas advanced spectroscopic techniques. The new information will guide our research on device fabrication and device matching efforts effectively.

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1. F. Zhu, J. Hu, I. Matulionis, T. Deutsch, N. Gaillard, A. Kunrath, E. Miller, A. Madan, *Amorphous silicon carbide photoelectrode for hydrogen production directly from water using sunlight*, Phil. Mag. B85, (2009) 1-16.
2. J. Hu, I. Matulionis, F. Zhu, J. Gallon, T. Deutsch, N. Gaillard, A. Kunrath, E. Miller, and A. Madan, Development of a photovoltaic (PV)/photoelectrochemical (PEC) hybrid device with amorphous silicon carbide as the photoelectrode for water splitting, MRS spring meeting, San Francisco, 2009.
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4. Y. Zhang, K. George, M. Bär, C. Heske, J. Hu, F. Zhu, and A. Madan, *Chemical and electronic structure of SiC thin films for photoelectrochemical water splitting*, MRS spring meeting, San Francisco, 2009.
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7. J. Kaneshiro, E. Miller, N. Gaillard and R. Rocheleau, *Advances in Copper Chalcopyrite Thin Films for Solar Energy Conversion*, to be published in Sol. Energy Mater. and Sol. Cells.

FIGURE 1. Current-voltage (JV) characteristics of CIGS₂ vs. CGSe₂ photocathodes vs. saturated calomel electrode under chopped simulated AM1.5G irradiance. Note that the CIGS₂ requires ~ 200 mV less to begin splitting water.

II.H.11 Critical Research for Cost-Effective Photoelectrochemical Production of Hydrogen

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Contract Number: DE-FG36-05GO15028

Subcontractors:

- Xunlight Corporation, Toledo, OH
- University of Toledo, Toledo, OH
- National Renewable Energy Laboratory, Golden, CO

Project Start Date: April 1, 2005

Project End Date: March 31, 2010

Objectives

- To develop critical technologies required for cost-effective production of hydrogen from sunlight and water using thin film (tf)-Si-based photoelectrodes.
- Two approaches are taken for the development of efficient and durable photoelectrochemical (PEC) cells:
 - An immersion-type PEC cell in which the photoelectrode is immersed in electrolyte.
 - A substrate-type PEC cell in which the photoelectrode is not in direct contact with electrolyte.

Technical Barriers

This project addresses the following technical barriers from the Photoelectrochemical Hydrogen Production section (3.1.4) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

(Y) Materials Efficiency

(Z) Materials Durability

(AB) Bulk Materials Synthesis

(AC) Device Configuration Designs

(AD) Systems Design and Evaluation

Technical Targets

This project focuses on the development of photoelectrode materials and tf-Si-based PEC cells required to achieve or exceed DOE's technical targets. The status of the project towards the DOE Multi-Year Program Plan objectives for Photoelectrochemical Production of Hydrogen for 2013 is listed in Table 1.

TABLE 1. Progress towards Meeting Technical Targets for Immersion- and Substrate-Type PEC Cells and Systems

Characteristic	Units	DOE 2012 Targets	MWOE 2009 Status
Solar-to-Hydrogen efficiency	% Efficiency	8	TBD
Durability	Hours	1,000	500*
Cost	\$ gge	2-3	TBD
Photocurrent of TCCR	mA/cm ²	8 (MWOE Target)	0.0214
Photocurrent of PAS	mA/cm ²	8 (MWOE Target)	23.0
Deposition Temperature	°C	250 (MWOE Target)	250
Transparency of TCCR	% Transmission	90 (MWOE Target)	90

TBD - to be determined

* tested on materials only (has to be confirmed for the PEC module)

The solar-to-hydrogen efficiency cannot be calculated until we deposit our optimum transparent, conducting and corrosion-resistant (TCCR) coatings or photo-active semiconductor (PAS) layer on a triple or tandem junction tf-Si solar cell, respectively, which is the next step in the development process. Cost analysis cannot be done until a module is fabricated and measurements are done. The last four targets are those outlined in the project objectives.

Accomplishments

- A 4"×12" substrate-type PEC cell was successfully tested and a 12"×12" model is under development.
 - Long-term stability tests for substrate-type PEC were conducted.
- TCCR and H₂ evolution catalysts were developed (Task 1).

- For use as TCCR material $\text{In}_2\text{O}_3\text{-Fe}_2\text{O}_3$ and $\text{In}_2\text{O}_3\text{-InFe}_2\text{O}_4$ are found most promising as these material classes are providing sufficient stability and excellent conductivity.
- A process for large-area electroplating of porous Ni as H_2 evolution catalyst has been developed.
- Fabrication and optimization of triple-junction, a-Si/a-SiGe/a-SiGe and a-Si/a-SiGe/nc-Si, and tandem, a-Si/nc-Si, photoelectrodes is pursued under Task 2.
 - Plasma treatments prior to device deposition have been found beneficial for improving device performance and long-term reliability.
- NREL team led by John Turner is developing improved understanding of PEC processes for a-Si-based photoelectrodes (Task 3).
- Task 4 focuses on the construction and optimization of deposition systems for fabricating large-area photoelectrodes used in immersion-type PEC cells.
 - Electroplated ZnO was successfully tested for use as textured back reflector.
- Facilities for large-area processing of substrate-type PEC cells have been established; processes for PEC components are under development (Task 5).
 - Sintered electrodes (Ni-Zn-Mo-Al) have been developed and tested regarding their usefulness as anodes.
 - Screen-printing techniques for applying current collection grids were optimized.
 - Photo-assisted electrochemical shunt passivation process for removing shunts and shorts in photoelectrodes was optimized.

Introduction

In this project, MWOE and its subcontractors are jointly developing the critical technologies required for cost-effective production of hydrogen from sunlight and water using tf-Si-based photoelectrodes. These triple-junction tf-Si-based electrodes include triple cells with either amorphous silicon germanium alloy (a-SiGe) or microcrystalline silicon ($\mu\text{c-Si}$) as the narrow band gap absorber material.

Two separate approaches have been pursued for the development of immersion- and substrate-type PEC photoelectrodes:

- In one approach, triple-junction tf-Si-based photoelectrodes (a-Si/a-SiGe/a-SiGe or a-Si/a-SiGe/ $\mu\text{c-Si}$) are used to generate the voltage bias necessary for hydrogen generation. A TCCR coating is deposited on top of the photoelectrode for

protecting the semiconductor layers from corrosion while forming an ohmic contact with the electrolyte.

- The second approach uses a hybrid structure, in which two tf-Si-based junctions (middle and bottom junctions of the present triple-junction tf-Si cell) provide a voltage bias of about 1.1 V, and a third junction (the top junction) forms a rectifying junction between a PAS and the electrolyte.

State-of-the-art a-Si/a-SiGe/a-SiGe and/or a-Si/a-SiGe/ $\mu\text{c-Si}$ devices are used as photoelectrodes. The corrosion resistance and PEC mechanisms for a range of oxide-, nitride- and carbide-materials, and II-VI compounds are under investigation. High-performance, durable PEC cells and systems will be developed, optimized and demonstrated in this project.

Approach

Five technical tasks are being performed under this grant in order to accomplish the project objectives:

- **Task 1:** Transparent, conducting and corrosion resistant coating for a triple-junction tf-Si-based photoelectrode.
- **Task 2:** Hybrid multi-junction PEC electrode having semiconductor-electrolyte junction.
- **Task 3:** Understanding and characterization of photo-electrochemistry.
- **Task 4:** Development of device designs for low-cost, durable and efficient immersion-type PEC cells and systems.
- **Task 5:** Development of device designs for large area, substrate-type PEC cells.

Results

Tasks 1 focuses on the preparation of TCCR coatings deposited onto the top of the tf-Si photoelectrode. During this reporting period emphasis was focused on the deposition of $\text{In}_2\text{O}_3\text{-Fe}_2\text{O}_3$ and $\text{In}_2\text{O}_3\text{-InFe}_2\text{O}_4$ films as these materials provide sufficient long-term and current density. The TCCR films were deposited using radio frequency magnetron sputter deposition in argon and oxygen using multiple sputter guns simultaneously. From the work completed, the results indicate that samples made at 250°C with 30 W of In and 100 W of InFe_2O_4 , and a sputter deposition time of 90 minutes produced optimal results. Photocurrent measurements indicate that the best sample displays a maximum current density J of $21.4 \mu\text{A}/\text{cm}^2$ at 0.65 V (Figure 1). However, the dark current is significant indicating crystallization inhibitions during film formation. Figure 2 shows the stability scans, current density-voltage (JV)-cycles between -1 V and +3 V for a sample sputtered at 30 W In and 100 W

FIGURE 1. Variation of In deposition power reaches a maximum at 30 W with 100 W InFe_2O_4 for 90 min deposition time.

FIGURE 2. JV-cycles (-1 V to +3 V) for TCCR sputtered with 30 W In and 100 W InFe_2O_4 (90 min deposition time).

InFe_2O_4 . Note that the JV-curve stabilizes after the first sweep.

Under Task 1 a method for large-area electroplating of porous Ni used as an H_2 -evolution catalyst has been developed. The method uses the co-deposition of Ni and Zn onto the back-side of tf-Si photoelectrodes, after Ni/Zn electrodeposition Zn is leached out leaving a porous Ni-structure behind.

Under Task 2 optimization work on tf-Si photoelectrodes used for hybrid PEC cells has been performed. During this reporting period major emphasis was focused on improving the device/substrate interface and in particular the interface between stainless steel and n-layer. It has been found that this interface determines significantly device adhesion and therefore device performance and long-term reliability. Plasma-etching steps before device deposition using H-, Ar- and Ar/O-plasma have been evaluated. JV-data obtained for tandem tf-Si photoelectrodes (a-Si/nc-Si) under illumination suggest that the device performance can be improved when using Ar or H_2 plasma treatments for conditioning the stainless steel substrate surface before tf-Si device deposition.

Task 3 focuses on the understanding of electrochemical processes of PEC cells and on the characterization of tf-Si photoelectrodes. MWOE collaborates with Dr. John Turner (NREL) in order to get a detailed understanding of a-Si/a-SiGe/a-SiGe and

FIGURE 3. JV-Curves of a-Si Devices With and Without Back-Reflector (BR)

a-Si/a-SiGe/ μ c-Si devices used as photoelectrodes in substrate and immersion-type PEC cells.

Efforts pursued under Task 4 emphasize the development of system designs and components used for immersion-type PEC cells. The incorporation of metallic reflective and transparent conductive back-reflector in photoelectrodes re-directs incident light into the tf-Si device. This effect increases conversion efficiency η , short-circuit current J_{sc} and fill factor (FF) of the device. Figure 3 shows the JV-curves of a-Si single junction devices with and without back-reflector. Although these cells are single devices, this is an important step towards fabricating multi-junction (tandem, triple) and semiconductor electrolyte junction photoelectrodes. Electrodeposition of ZnO for use as textured back-reflector was tested. Initial results indicate the feasibility of this process for back-reflector fabrication although further process optimization is necessary for obtaining high quality, diffuse reflective ZnO layers.

Task 5 focuses on the development of processing procedures for large-area photoelectrodes. Under this task sintered electrocatalysts employed as anodes in substrate-type PEC cells were developed. Metal powder mixtures containing Ni with different amounts of Zn, Al, Mo were sintered at 800°C in order to form porous electrodes. JV-measurements performed in potassium hydroxide as electrolyte suggest the feasibility of using these material combinations as porous anodes or cathodes.

During this reporting period several reliability and performance improvements for large-area photoelectrodes were accomplished. It has been found that improvements in the current collection grid design leads to a significant reduction in series resistance yielding for improved device performance. The optimized current collection grid uses a screen printed collector and tin-clad copper foil collector buses.

The state-of-art light-assisted shunt passivation process for large-area photoelectrodes lead previously to reliability issues when using a metallic back-reflector layer inserted between the stainless steel substrate and photovoltaic device. Process and reliability improvements were accomplished by varying the electrolyte used for electrolytic passivation. The improved procedure allows processing with less corrosive metal salts.

Conclusions and Future Directions

The proposed future work will include:

- Continue optimization of present oxide materials suitable for TCCR coatings:
 - Material class studies are focusing on In_2O_3 - Fe_2O_3 and In_2O_3 - InFe_2O_4 providing most promising stability and conductivity.
- Develop chemical plating for materials suitable for PAS and TCCR coatings for immersion-type hybrid PEC cells.
- Leveraging our resources on building a prototype for large-area (1ft×1ft) substrate-type PEC.
 - Design of final substrate-type PEC will employ porous Ni as H_2 evolution catalyst electroplated onto the backside of stainless steel substrates with a triple junction a-Si device on the front-side.
 - Long-term reliability studies and solar-to- H_2 -efficiency measurements will be performed.
- Develop 4"×4" immersion-type PEC cells:
 - Long-term reliability studies and solar-to- H_2 -efficiency measurements will be performed.
- Improve performance of large-area photoelectrodes.

- Complete techno-economic and energy analyses for PEC systems for hydrogen production.

FY 2009 Publications/Presentations

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2. Zhang, S.; Liao, X.; Fan, Q.H.; Xiang, X.; Adiga, N.; Ingler Jr., W.B.; Du, W.; Cao, X.; Deng, X.: "*Impacts on n-type Interface on the Performance of a-Si Based Solar Cells*" 34th IEEE PVSC, 2009.
3. Ingler Jr., W.B.; Ong, G.; Deng, X.: "*RF Sputter Deposition of Indium Oxide - Iron Oxide Films for Photoelectrochemical Hydrogen Production*" ECS Trans. Vol. 16, No. 7. (State-of-the-Art Program on Compound Semiconductors 49 (SOTAPOCS 49), 2008, 49.
4. Ingler Jr., W.B.; Ong, G.; Deng, X.: "*RF Sputter Deposition of Indium Oxide - Iron Oxide Films for Photoelectrochemical Hydrogen Production*" ECS Trans. Vol. 16, No. 7. (State-of-the-Art Program on Compound Semiconductors 49 (SOTAPOCS 49), 2008, 49. 210th Meeting of the Electrochemical Society, Inc., Honolulu, HI, October 12–17 (Oral Presentation).
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II.H.12 Photoelectrochemical (PEC) Hydrogen Generation*

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Contract Number: DE-FC36-06GO8654

Cost-Sharing Partner:
Arkansas Science and Technology Authority,
University of Arkansas at Little Rock, Little Rock, AR

Project Start Date: July 1, 2006
Current Project End Date: August 1, 2009.

*Congressionally directed project

- Develop a hybrid semiconducting photoanode, TiSi_2 , with a corrosion inhibiting TiO_2 protective layer.
- Use heterogeneous, nanostructured, and hybrid semiconductor photoanodes consisting of layered electrodes made of TiSi_2 and TiO_2 for electrolyzing water.
- Perform fundamental studies on surface energetics: (a) control of surface states, (b) minimization of traps that are responsible for recombination of photo-excited charge carriers at the interface, and (c) reduction of photocorrosion of semiconductor electrodes.
- Design and construct a prototype hydrogen generator for demonstration.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (Y) Materials Efficiency
- (Z) Materials Durability
- (AC) Device Configuration Designs

Technical Targets

Our technical target is to reach the DOE goals:

- Chemical conversion process efficiency: 10% by 2010 and 12% by 2015
- Plant STH efficiency: 8% by 2010 and 10% by 2015
- Hydrogen production cost: \$3.00/gge (approximately 1 kg of H_2) by 2018

The band gap of the semiconductor electrode needed in PEC electrolysis must not be higher than 2.5 eV in order to harvest the bulk of the solar flux which resides within the wavelength range 350 to 800 nm, and the band-edge of the semiconductor must straddle the electrochemical redox potentials of water [1,2]. The semiconducting electrode must be corrosion-resistant in contact with the electrolytes used in the PEC cell for splitting water. However, most stable semiconducting electrodes have large band gaps and hence low efficiency for photo-conversion for the entire spectrum of solar radiation. Reduction of band gap by doping the bulk of the semiconductor has not been found successful since such a process introduces charge carrier traps and compromises electron conduction and

Objectives

The goal is to produce hydrogen economically using photoelectrochemical (PEC) electrolysis of water directly from sunlight with corrosion resistant semiconductor electrodes for catalytic conversion. The specific objectives are:

- Improve (a) photo-conversion efficiency (solar-to-hydrogen [STH] ratio) to 10 percent evolving H_2 and O_2 and (b) photo-corrosion resistance of photoanodes for 5,000 hours of operation generating H_2 from water.
- Synthesize photoanodes maximizing both light absorption and photoactive sites for high STH conversion.
- Develop surface engineered TiO_2 and TiSi_2 nanostructured photoanodes (nanotubes and nanorods) doped with N, to reduce the effective band gap.

material durability. Small band gap electrodes suffer from poor stability, inadequate charge transfer properties and a high charge recombination rates.

The primary focus is to develop photoanodes with high photo-conversion efficiency in order to develop PEC-based hydrogen generators that are scalable, financially attractive in the global economy, and environmentally safe.

Accomplishments

- Titanium disilicide (TiSi_2) thin films as a part of composite multilayer high efficiency photoanodes for hydrogen generation have been synthesized.
- Electrochemical synthesis of patterned TiO_2 nanorods and nanotubes with separations comparable to wavelength of visible light for trapping solar radiation.
- Multi-layered photoanodes for high efficiency photo-conversion and minimization of photocorrosion.
- Plasma treatments of photoanodes for (a) removing charge traps, (b) surface doping with nitrogen, and (c) creating oxygen vacancies for achieving high photocurrent density.
- Design of prototype PEC hydrogen generator with a solar radiation concentrator for optimized operation.

Approach

- (1) We used TiO_2 photoanodes for its stability, inertness and cost effectiveness, in our investigations on (a) the development of nanostructured photoanodes, (b) surface doping with N, (c) plasma treatments for removing surface contaminants, (d) reducing traps of interfacial charge carriers, and (e) optimization of photocurrent density.
- (2) Since the band gap of TiSi_2 semiconductor electrodes varies over a wide range from 1.5 eV to 3.4 eV, our approach during this year has been on the use TiSi_2 for electrolyzing water.
- (3) A thin layer of TiO_2 semiconductor needs to be applied as a protective cover over the TiSi_2 layer for inhibiting corrosion. TiO_2 is one of the most stable semiconductors for PEC application but its wide bandgap allows harvesting photons only in the ultraviolet range.
- (4) The interfacial charge transfer process between the layered semiconductors will be optimized by controlling the thickness of the films to match the width of the charge depletion layers and by plasma surface treatments. Both TiSi_2 and TiO_2 are good

electron conductors; hence minimal recombination losses are expected when penetration depth is made equal to the film thickness and the width of the charge depletion layer.

- (5) Our approach has been to use patterned nanotubular electrodes that maximizes both light absorption efficiency and interfacial sites for oxidizing water. Based on our studies, we are synthesizing triple layer nanotubular arrays with wall thickness comparable to the diffusion length of the holes. The outer surface of the nanotubular electrodes is to be plasma treated with nitrogen in order to create oxygen vacancies at the outer surface layer forming TiN and to increase the height of the charge depletion layer.
- (6) We are currently testing the photo-corrosion resistance of TiO_2 and TiSi_2 photoanodes using electrochemical impedance spectroscopy under ultraviolet and visual radiation exposures. We will test and evaluate the prototype hydrogen generator following the standard test protocol developed by the DOE PEC working group.
- (7) Our approach has been focused on the design and construct of an integrated laboratory scale self-standing PEC-based hydrogen generators using heterogeneous, nanostructured hybrid layered electrodes made of TiSi_2 and TiO_2 semiconductors with solar concentrators (Figure 1).

Results

- Development of titanium disilicide thin films as a part of composite multilayer high efficiency photoanodes for hydrogen generation (Figures 2, 3).
- Deposition of thin layer of TiSi_2 (Figure 2).

FIGURE 1. Design of an Integrated Laboratory Scale Hydrogen Generator using Stacked PEC Cells and Solar Concentrator

FIGURE 2. Scanning Electron Microscope Image of a Titanium Silicide Film on a Silicon Substrate

FIGURE 3. Application of layered photoanodes using TiSi_2 and TiO_2 semiconductors. TiSi_2 electrode with coating of a transparent TiO_2 electrode to be used for studying the PEC activities.

- Development of patterned nanotubular structure by ramping voltage during electrochemical anodization process (Figure 4).
- Design of two-layer nanotubes of TiO_2 and TiSi_2 (Figure 4).
- Nanotube fabrication with stepped voltage anodization (Figure 5).
- Optimization of nitrogen plasma treatment process for maximizing photocurrent density.
- Optimization of the annealing process for nanotubular electrodes.
- Plasma surface modifications have shown to minimize the presence of hole traps at the interface and provide remarkable increase in photocurrent density.
- Design of PEC-based hydrogen generator with photoanodes consisting of layered electrodes made of TiSi_2 and TiO_2 for electrolyzing water (Figure 6).

Conclusions and Future Directions

The present work reports the importance of systematic investigations of (1) the geometric structure of the nanotube arrays, (2) the plasma process for surface doping of TiO_2 nanotubular photoanode

FIGURE 4. Current transient during anodization of Ti while ramping the voltage from 60 V to 20 V.

FIGURE 5. Design of two-layered nanotubes in packed form with their outer walls in contact with each other (top) and two-layered nanotubes with their walls separated from each other with spacing equal to the wavelength of incident light (bottom). The separation between the walls traps incident light for improved absorption.

with N for decreasing surface bandgaps and (3) annealing process for crystallization for improving photocatalytic generation of hydrogen by splitting water. TiO_2 nanotubular photoanodes can be prepared by anodization of a titanium foil in an electrolyte containing ethylene glycol, ammonium fluoride, and distilled water. The diameters of the nanotubes were varied by adjusting the anodization voltage and the length of the nanotubes were varied by varying the time period of anodization. Conical shaped nanotubes with their bases larger than the diameter of their tips were prepared by anodizing at stepped voltages

FIGURE 6. Scanning electron microscope image showing the three layer of TiO_2 nanorods formed when the anodization was carried out by ramping the voltage from 60 to 20 Volts.

60 V–40 V–20 V volts for a total time period of 60 min. Nanotubular structure of TiO_2 photoanodes prepared at stepped voltages showed 55% improved photocurrent density compared to the anodic structures prepared by constant voltage anodization.

The present studies also showed that plasma surface doping in nitrogen atmosphere is very effective for improving photocurrent density. Plasma surface doping of TiO_2 nanotubular photoanodes for 20 min showed 80% improvement of photocurrent density measured under the same condition but without plasma treatment process. In sum, the test results show promising aspects of tuning several parameters involved in photoelectrochemical processes in improving conversion efficiency. The structural aspects and surface chemistry both influence greatly the efficiency of solar energy conversion in photocatalytic and photovoltaic processes.

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2. Rajesh Sharma, Jacob P. Bock, Alexandru S. Biris, Malay K. Mazumder, Prajna P. Das, Manoranjan Misra, Vishal K. Mahajan, "Evaluation of atmospheric-pressure plasma for improving photo electrochemical response of titania photoanodes," *IEEE Transactions on Industry Applications*, 2009. [In Press]
3. Hidetaka Ishihara, Jacob P Bock, Rajesh Sharma, Franklin Hardcastle, Alexandru S Biris, and Malay K Mazumder, "Electrochemical synthesis of titania nanotube array for photoelectrochemical hydrogen production," in *Proc. Electrostatic Society of America Annual Meeting*, Boston, MA, June 16–19, 2009.

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II.H.13 University of Nevada, Reno Photo-Electrochemical Project*

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Projected End Date: September 30, 2009

*Congressionally directed project

Technical Barriers

This project addresses the following technical barriers from the Production section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (Y) Materials Efficiency
- (Z) Materials Durability

Technical Targets

This project is investigating potential application of hybrid TiO₂ nanotubes for hydrogen generation by water photoelectrolysis. Insights gained from these studies will be applied toward the design and synthesis of high efficiency materials for hydrogen generation from water splitting that meet the following DOE targets:

- Usable semiconductor band gap: 2.3 eV by 2013.
- Chemical conversion process efficiency: 10% by 2013.
- Plant durability: 1,000 hrs by 2013.

Approach

In this project, utilization of hybrid metal (Ti, W, Fe, and Ta) oxide nanotubular arrays for generation of hydrogen from water using sunlight is studied. The nanotubular arrays are prepared by sonoelectrochemical anodization of the respective metals in optimized synthesis conditions. We have already developed processes to synthesize metal oxide nanotubes in inorganic, organic and ionic liquids as electrolytes. This process is suitable to prepare mixed metal oxide nanotubes e.g. TiFe, TiMn and TiW. In addition to the anodization process, we are developing new mixed metal oxide compounds by electrodeposition, hydrothermal and microwave assisted methods. This project is integrating a highly efficient photoanode, a cathode, and a modified electrolyte to design a photoelectrochemical cell (PEC) to generate hydrogen with at least 10% efficiency by 2013. The scale-up and stability of the materials looks highly promising for large scale hydrogen generation. It is envisioned that the process can be efficient and economical in the production of solar hydrogen.

The hydrogen generation work is conducted using a hybrid metal oxide or mixed metal oxide nanotubes electrode in alkaline solutions in the presence of simulated and on-field solar light. The photo-efficiency is determined by measuring current as well as volume of

Objectives

- Develop high efficiency metal oxide nanotubular array photo-anodes for generating hydrogen by water splitting.
- Develop density functional theory to understand the effect of morphology of the nanotubes on the photo-electrochemical properties of the photo-anodes.
- Develop kinetics and formation mechanism of the metal oxide nanotubes under different synthesis conditions.
- Develop combinatorial approach to prepare hybrid photo-anodes having multiple hetero-atoms incorporation in a single photo anode.
- Improve the durability of the material.
- On-field application.
- Scale-up the laboratory demonstration to production unit.

the hydrogen generated using water displacement and gas chromatography analysis. The material stability and photo-efficiency is determined as a function of time, electrochemical and analytical measurements.

In the future our main focus for the research will be to understand:

1. Synthesis of visible light active mixed metal oxide photocatalysts.
2. The formation mechanism and kinetics of metal oxide.
3. Reaction kinetics of the water splitting reactions at the interface.
4. Effect of nanotubular wall thickness on electron trapping.
5. Effect of band bending across the nanotube wall.
6. Stability of the catalysts for 1,000 hrs.

On the basis of fundamental and applied research, a scale-up experiment in the laboratory will be performed to elucidate the viability of the new catalysts for PEC generation of hydrogen using sunlight.

Accomplishments

- The UNR team has developed a novel sonoelectrochemical process to prepare smooth and ultra-thin hematite band gap (2.2 eV) nanotube arrays (Figure 1). We have also developed a process to prepare TaON nanotube arrays (band gap 2.07 eV). These materials showed excellent visible light activity compared to TiO_2 nanotubes (Table 1).
- UNR also designed a PEC cell for on-field hydrogen generation (Figure 2).

FIGURE 1. Scanning Electron Microscope Images of: (A) & (B) Fe_2O_3 Nanotubes and (C) TaON Nanotube Arrays

TABLE 1. Comparison of Photocurrent Density of TaON Nanotubes with Various other Photocatalysts

Photocatalyst	Photocurrent density (mA/cm^2) at 0.5 V _{Ag/AgCl}	Visible Light Contribution (%)
P25/Ti	0.365	0.32
TiO_2 NTs/Ti	0.638	0.39
Fe_2O_3 NTs/Fe	1.4	50
Fe_2O_3 nanoparticle/Fe	0.004	NA
Ta_2O_5 NTs/Ta	0.25	0.28
TaON NTs/Ta	2.6	47

FIGURE 2. Preliminary results indicate that H_2 generation from on-field experiments is comparable to the experiments under simulated solar light conditions (AM 1.5).

Conclusions and Future Actions

- In the last year, we have synthesized photoanodes with low band gap nanotubular materials by sono-electrochemical anodization techniques. We have also expanded the idea to understand the formation mechanism, crystallization and kinetics of the formation of nanotubes by the sono-electrochemical anodization method. These nanotubes are found to be efficient materials for hydrogen generation by water splitting using visible light. These nanotubular photo-anodes are found to be stable for 30 days (8 h/day). In summary, the following bulleted list is indicative of the areas we will pursue in the coming year of the project:
- Synthesis of one dimensional mixed metal oxide and metal oxynitride nanotubular materials.
- Synthesis of coupled and combinatorial photo-anodes.
- Incident photon to current conversion efficiency measurements.
- Design large PEC system for on-field testing under real solar irradiation.
- Scale-up testing for solar light harvesting.

Special Recognitions & Awards/Patents Issued

1. "Preparation of nanotubular titania substrate with oxygen vacancies and their use in photo-electrolysis of water", US patent, PCT/US2006/035252.
2. "Preparation of nano-tubular titania substrates having gold and carbon particles deposited thereon and their use in photo-electrolysis of water", US patent PCT/US2008/060293.

FY 2009 Publications/Presentations

Publications

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12. "Nanostructured anodic iron oxide film as photoanode for water oxidation" *J. Physics D: Appl. Phys.*, 42 (2009) 135303 (10pp).

Presentations

1. "Photooxidation of Water Using Vertically Aligned Nanotube Arrays: A comparative study of TiO₂, Fe₂O₃ and TaON nanotubes" Material Research Society Meeting 2009, March 16th, San Francisco, CA.
2. "Nanotubular semiconductor photocatalysts for visible light water photooxidation: UNR update" PEC Working Group Meeting 2009, March 17th to March 19th, San Francisco, CA.

II.I.1 Technoeconomic Boundary Analysis of Photobiological Hydrogen Producing Systems

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No. AFH-8-88601-01

Subcontractor:
Chuck Dismukes, Princeton, NJ

Project Start Date: April 15, 2008
Project End Date: August 31, 2009

Objectives

- Develop conceptual system designs for photobiological, dark fermentation and microbial electrolysis hydrogen production systems.
- Leverage strengths of each production method to create integrated hydrogen producing systems that improve upon individual systems.
- Calculate capital costs, operating costs and feedstock costs for conceptual systems.
- Compute levelized hydrogen costs for conceptual design.
- Determine key factors affecting cost estimates.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (AK/AQ) Diurnal Operation Limitations
- (AJ/AP) Systems Engineering
- (AS) Waste Acid Accumulation

Technical Targets

This project is conducting systems engineering analysis for biological hydrogen (H₂) production. These studies and their results support the accomplishment of Hydrogen Production section milestones from the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan, namely:

- Milestone 45: Projected hydrogen production cost of less than \$4/kg for photolytic hydrogen production.
- Milestone 46: Projected durability of 5,000 hours and cost of hydrogen of \$50/gge.
- Milestone 54: Projected hydrogen production cost of less than \$4/kg for photosynthetic bacterial hydrogen production.
- Milestone 57: Projected hydrogen production cost of less than \$4/kg for dark fermentative hydrogen production.

Accomplishments

- Developed conceptual designs of biological hydrogen plants with sufficient detail to estimate hydrogen costs from such systems and compare on an equal basis those costs to other production costs from other methods.
- Hydrogen from the most cost-effective standalone system is approximately \$2.99/kg.
- Explored synergies between various biological hydrogen production methods to design and evaluate integrated systems.
- Hydrogen from the most cost-effective integrated system is \$3.21/kg.
- Concluded that the primary factor affecting hydrogen costs from these systems is plant size.
- Concluded that only in the systems utilizing acetic acid are nutrients a substantial cost.

Introduction

This project considered multiple pathways for the biological production of gaseous hydrogen, including photobiological H₂ production from a variety of genetically engineered algae and bacteria, dark fermentation of waste photobiological organisms, dark fermentation of lignocellulosic biomass, and the microbial electrolysis of fermentative waste.

Additionally, the integration of multiple systems was considered for added hydrogen production and reduced cost. Within the analysis, five different photobiological organisms, three different fermentative pathways, and three different integrations of these systems were examined. Those organisms and systems are described in Table 1.

TABLE 1. Organisms and Systems Analyzed

Pathway	Description
Photobiological	
B-1	A truncated antennae Chlamydomonas mutant with an oxygen-tolerant hydrogenase
B-2	A truncated antennae Cyanobacteria mutant with an oxygen-tolerant hydrogenase
B-3	A sulfate-permease Chlamydomonas mutant with a truncated antennae
B-4	An immobilized, sulfur-deprived Chlamydomonas mutant with a truncated antennae
B-5	A truncated antennae Purple Non-Sulfur (PNS) photosynthetic bacterial mutant
Fermentative	
C-1, C-2, C-5	H ₂ production using dark fermentation of photobiological systems algal waste
Lignocellulosic Fermentation	H ₂ production using dark fermentation of lignocellulosic feedstock (corn stover)
MEC	H ₂ production from a Microbial Electrolysis Cell (MEC) using fermentation waste as a feedstock.
Integrated	
Stacked Beds (B-3/B-5)	Integration of Chlamydomonas and PNS photobiological systems for added hydrogen production due to fuller use of the light spectrum.
Photobio/ Fermentation (B-1/C-1, B-2/C-2, B-5/C-5)	Integration of photobiological systems with the fermentation of their waste
Lignocellulosic-MEC	Integration of Lignocellulosic fermentation and MEC that consumes the fermentative waste of fermentation as the MEC feedstock

Approach

For each of the photobiological systems, hydrogen production characteristics were defined, individual reactors conceptually designed, and levelized hydrogen costs calculated. Concepts, biological parameters, and

FIGURE 1. Hydrogen Cost Variation with Plant Size

current experimental data were provided by the National Renewable Energy Laboratory (NREL) Biological Hydrogen Working Group. However, organism performance was based on the author's projection of future genetically modified organisms rather than current laboratory experimental measurements. The analysis was based on developing a large plant size from several smaller modules. Each module was sized for 1 tonne/day (TPD) H₂ production with large quantities of similar components within a single module. Additional capital cost reductions as a result of increased purchase quantities are not likely thus, capital costs of larger plants increase linearly. Labor is a large contributor to the final cost of the hydrogen produced. Figure 1 shows most of the cost benefit is gained in the initial increase in plant size. Thus, a 10 TPD plant size was chosen for cost analysis.

For each fermentative system, a plant design was selected, its capital cost and performance were estimated, and resulting levelized hydrogen cost computed. The design and performance of the waste algae fermentation plants was based upon research conducted by NREL on fermentative organisms [1-3], and corresponds to projections of future optimized performance. The design and performance of the microbial electrolysis cell (MEC) plant draws heavily from the concepts and laboratory work conducted at Penn State University [4-7]. The design of the lignocellulosic fermentation plant was based largely on a detailed NREL report analyzing the performance and cost of ethanol production from corn stover [8]. Fermentation for ethanol production and fermentation for hydrogen production share many characteristics. Consequently, the current project work product was greatly enhanced by making use of this analogous analysis.

For the integrated systems, different combinations of the biological H₂ production pathways were examined. Costs associated with these integrations as compared to the individual systems were evaluated. Four systems that

have sufficient synergies to make integration a possibility were chosen for analysis.

Results

Given the systems listed previously, the feasibility, performance, capital cost, and resultant \$/kg H₂ were evaluated for each stand-alone and integrated system. System hydrogen production costs are summarized in Table 2.

TABLE 2. H₂ Production Costs

System	kg H ₂ /day	\$/kg
Photobiological H₂ Production		
B-1 - Algal O ₂ -tolerant Hydrogenase	10,000	\$2.99
B-2 - Cyanobacterium O ₂ -tolerant Hydrogenase	10,000	\$2.99
B-3 - Algal Sulfate Permease	10,000	\$4.17
B-4 - Immobilized Algal, Sulfur deprived	10,000	\$6.02
B-5 - PNS Bacteria	10,000	\$10.36
Fermentation of Waste Algae/Photobacteria		
C-1 and C-2 - Effluent from B-1 and B-2	7	\$172.73
C-5 - Effluent from B-5	19	\$66.17
Fermentation of Lignocellulose - No byproduct credit	37,181	\$4.33
Fermentation of Lignocellulose - \$0.12/kg value of byproduct	37,181	\$2.09
MEC - Microbial Electrolysis Cell - Acetic Acid Feedstock	88,055	\$12.43
Integrated Photobiological - B-3/B-5 Stacked	10,600	\$5.25
Integrated Photobiological/Fermentor		
B-1/B-2 & C-1/C-2 Integration	10,007	\$3.21
B-5 & C-5 Integration	10,019	\$11.04
Integrated Lignocellulosic Fermentor/MEC	125,266	\$6.61

For the pure photobiological systems, B-1 and B-2 achieved the lowest costs, however, these results are predicated on major improvements in organism mutations achieving truncated antenna reductions, elimination of cell light saturation due to electron transfer rate limits, and successful operation of the reactor bed design. The B-3 and B-4 system costs are slightly higher and the systems are more complex, but the components have been more completely demonstrated. The B-5 system has the highest cost of the photobiological systems due the higher number of photons needed (11 to 15 vs. 4) to generate each H₂ molecule and the high cost of the acetic acid feedstock.

A sample of the plant design of a photobiological plant is shown in Figure 2.

The algae/bacteria fermentation systems have high costs due to the low organism feedstock input resulting in low H₂ output. A large part of the resulting H₂ cost is due to the labor (94-96% of total cost) since it is analyzed as a stand-alone system. The cost contribution of the labor drops drastically when integrated with a photobiological system. The results are based on a projected fermentation output of highly sulfur-deprived organisms and do not fully exploit the organic components of the algae feedstock. It is expected that future bacteria and processing developments could facilitate more extensive conversion of the starch, lipid and protein content of the algae into H₂.

The lignocellulosic fermentation achieved a moderately low H₂ cost, using bacteria and processing that has been proven in lab environments, but not in large scale demonstrations. There is also a high potential for cost reduction from the sale of the 51% acetic acid content liquid byproduct. If the byproduct had a market value of \$0.12/kg (as compared to the market price of ~\$0.60/kg for acetic acid [9]), the net H₂ cost would be reduced to nearly \$2.00/kg.

For the MEC system, the moderately high H₂ cost resulted from the very dilute acetic acid/water reactant, and necessitated a very large reactor volume and correspondingly very large anode and cathode areas. This high capital cost was coupled with high acetate market price, which could potentially be reduced by lowering acetic acid purity, which is not marketed, but is available as a fermentor byproduct. The immaturity of the full-scale system concepts and components indicated that there is extensive potential for future cost reductions. Cost saving could also arise from higher concentration of electrolyte and higher pressure operation.

For the integrated, stacked photobiological system, the H₂ cost is between the cost of the two individual stand-alone systems. For the integrated photobiological algae/fermentor system, the H₂ costs are higher than the stand-alone photobiological system. For the integrated fermentor/MEC system, the MEC's H₂ production cost is reduced significantly due to the free feedstock. However, due to high MEC capital costs, the cost of the combined system is still significantly higher than the fermentor alone. In all of these systems there is no cost benefit to integration.

Conclusions and Future Directions

The analysis portion of this project was completed at DTI during the 2nd quarter of 2009. Incorporation of comments to the final report remains. Although the knowledge gained from this analysis was of great

FIGURE 2. B-1 Plant Design

benefit, further studies are recommended to improve the understanding of how these systems can contribute to the hydrogen transition.

- Future Photobiological Systems analyses recommended are:
 - Validation of future performance projections with experimental data.
 - System evaluation using alternative reactor bed concepts.
 - Analysis of a B-4 system with an alternative immobilization mat, made of alginate, which can be used as fermentor feedstock so these two systems can be integrated.
- Future Algae Fermentation Systems analyses recommended are:
 - Evaluation of pre-treatment processes to significantly increase the algae-to-hydrogen conversion rate.
 - Modification of algae feedstock characteristics so that it is better suited for fermentation.
- Reduction in fermentation process duration to assess impact on costs.
- Future Lignocellulose Fermentation Systems analyses recommended are:
 - Verification of byproduct market demands, prices and supply to validate H₂ production costs.
 - Detailed design of byproduct component separation (acids, ethanol, etc.).
- Future MEC Systems analyses recommended are:
 - Optimization of process and components for low capital cost systems.
 - Correlation of ion transport loss to reactor size.
- Future Integrated Systems analyses recommended are:
 - Exploration of additional combinations to achieve reduced hydrogen cost.
 - Modification of reactor bed configurations for the purpose of improving the integrated system costs.

FY 2009 Publications/Presentations

1. Deliverable 4.4.3. Draft Final Report. Contract Milestone Report. 24 June 2009.
2. 2009 DOE Hydrogen Program Review - Washington, DC - May, 2009. Presentation PD# 15.
3. Deliverable 4.3.1. Task C Part II: Lignocellulosic Fermentative H₂ Production Subsystems Results & Discussion. Contract Milestone Report. 17 April 2009.
4. Deliverable 4.2.2. Task B: Photobiological H₂ Production Subsystems Combined Report, Characterization & Results. Contract Milestone Report. 23 January 2009.
5. Deliverable 4.2.1. Task B: Photobiological H₂ Production Subsystems Characterization Report. Contract Milestone Report. 24 December 2008.

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II.1.2 Maximizing Light Utilization Efficiency and Hydrogen Production in Microalgal Cultures

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Contract Number: DE-FG36-05GO15041

Start Date: December 1, 2004
Projected End Date: November 30, 2010

Objectives

- Minimize, or truncate, the chlorophyll (Chl) antenna size in green algae to maximize photobiological solar conversion efficiency and H₂ production.
- Demonstrate that a truncated Chl antenna size would minimize absorption and wasteful dissipation of sunlight by individual cells, resulting in better light utilization efficiency and greater photosynthetic productivity by the green alga mass culture.

Technical Barriers

This project addresses the following technical barriers from the Production section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

(AG) Light Utilization Efficiency

Technical Targets

The Hydrogen, Fuel Cells and Infrastructure Technologies Multiyear Program Plan technical target for 2005 for this project was to reach a 10% utilization efficiency of absorbed light energy (out of a theoretical maximum of 30% possible) in unicellular green. Progress has currently achieved a green alga utilization efficiency of absorbed light energy of about 25%.

Approach

- Employ deoxyribonucleic acid (DNA) insertional mutagenesis, screening, biochemical and molecular genetic analyses for the isolation of “truncated Chl antenna size” mutants in the green alga *Chlamydomonas reinhardtii*.
- Clone and characterize the gene(s) that affect the “Chl antenna size” property in *Chlamydomonas reinhardtii*.
- Apply such genes to generate a “truncated Chl antenna size” in this and other green algae.

Accomplishment

- Published manuscript on the utility of the *Tla1* gene in conferring a truncated chlorophyll antenna size and on the mechanism by which it maximizes light utilization efficiency and hydrogen production in microalgal cultures.
- Isolated and characterized new “truncated chlorophyll antenna size” mutants *tla2* and *tlaR*. Properties of these strains are given in Tables 1 and 2.

TABLE 1. *Chlamydomonas reinhardtii* cellular chlorophyll content, photosystem chlorophyll antenna size and energy utilization efficiency in wild type, *tla1*, *tla2* and *tlaR* mutant mutant strains, as determined by spectrophotometric kinetic analysis (n = 5, ±SD).

	wild type (WT)	<i>tla1</i>	<i>tla2</i>	<i>tlaR</i>	Long-term goal
Chl/cell mol x10 ⁻¹⁵	2.4 ±0.5	0.9 ±0.06	0.93 ±0.1	0.7 ±0.1	
Chl-PSII	222 ±26	115 ±36	80 ±30	50 ±30	37
Chl-PSI	240 ±4	160 ±12	115 ±10	105 ±10	95
Light Utilization Efficiency (Solar to Chemical)	~3%	~10%	~15%	~25%	~30%

TABLE 2. Progress achieved vs the DOE targets: utilization efficiency of incident solar light energy, E₀x E₁, %.

Year	2000	2003	2005	2008	2010	2015
Program Targets	3%	10%*			15%	20%
Actual Progress Achieved	3% WT	10% tla1	15% tla2	25% tlaR		

* Target adjusted upward to match ahead-of-schedule progress achieved.

Introduction

The goal of the research is to generate green algal strains with enhanced photosynthetic productivity and H_2 production under mass culture conditions. To achieve this goal, it is necessary to optimize the light absorption and utilization properties of the cells [1-4]. A cost-effective way to achieve this goal is to reduce the number of Chl molecules that function in the photosystems of photosynthesis. Thus, efforts are under way to isolate microalga mutants with a truncated chlorophyll antenna size.

The rationale for this research is that a truncated light-harvesting Chl antenna size in green algae will prevent individual cells at the surface of the culture from over-absorbing sunlight and wastefully dissipating most of it (Figure 1). A truncated Chl antenna size will permit sunlight to penetrate deeper into the culture, thus enabling many more cells to contribute to useful photosynthesis and H_2 production (Figure 2). It has been shown that a truncated Chl antenna size will enable about 3-4 times greater solar energy conversion efficiency and photosynthetic productivity than could be achieved with fully pigmented cells [5].

Approach

The focal objective of the research is to identify genes that control the Chl antenna size of photosynthesis and, further, to elucidate how such genes confer a truncated Chl antenna size in the model green alga *Chlamydomonas reinhardtii*. Identification of

such genes in *Chlamydomonas* will permit a subsequent transfer of this property, i.e., “truncated Chl antenna size”, to other microalgae of interest to the DOE Hydrogen Program. This objective is currently being approached through DNA insertional mutagenesis/screening and biochemical/molecular/genetic analyses of *Chlamydomonas reinhardtii* cells.

Results

The *tla2* mutant plasmid insert site has been cloned and a gene of interest has been tentatively identified as causing the *tla2* mutation. This molecular and genetic analysis is currently in progress. Work further described the isolation and biochemical and physiological characterization of a new mutant of *Chlamydomonas reinhardtii*, termed *tlaR*, having a truncated light-harvesting chlorophyll antenna size. Properties of the *tla* “truncated Chl antenna size” strains so far isolated are summarized in Tables 1 and 2, Figure 3. The *tlaR* mutant has the smallest yet Chl antenna size known in green algae. State-of-the-art was summarized in a review article by Mitra and Melis [4].

Future efforts will be directed toward the cloning and characterizing the genes responsible for the *tla* phenotype in *tla2* and *tlaR* mutants.

Conclusions

- Significant, ahead-of-schedule progress was achieved in terms of acquiring “truncated Chl antenna size” mutants. *This demonstrates feasibility of the approach chosen and success of the methods employed.*

FIGURE 1. Schematic presentation of the fate of absorbed sunlight in fully pigmented (dark green) algae. Individual cells at the surface of the culture over-absorb incoming sunlight (i.e., they absorb more than can be utilized by photosynthesis), and ‘heat dissipate’ most of it. Note that a high probability of absorption by the first layer of cells would cause shading of cells deeper in the culture.

FIGURE 2. Schematic of sunlight penetration through cells with a truncated chlorophyll antenna size. Individual cells have a diminished probability of absorbing sunlight, thereby permitting penetration of irradiance and H_2 -production by cells deeper in the culture.

FIGURE 3. Project timeline and publications record on the truncated chlorophyll antenna size project. Arrows show publication year of peer-reviewed paper for each of the truncated Chl antenna size mutants. Note that work with the *tla2* and *tlaR* strains has not yet reached the stage of a peer-reviewed paper.

- A truncated light-harvesting chlorophyll antenna size in the *tla*-type mutants enhanced solar conversion efficiencies and photosynthetic productivity under bright sunlight conditions.
- Insights on the molecular mechanism for the regulation of the Chl antenna size by the *Tla1* gene were obtained (results not shown pending publication of these findings in a peer reviewed journal).

Future Directions

- Advance the biochemical and molecular characterization of the *tla2* and *tlaR* strains.
- Clone the genes that confer the *tla2* and *tlaR* phenotypes.
- Establish transformation (sense and antisense) protocols with *Tla*-type genes to enhance the down-regulation of the Chl antenna size in *Chlamydomonas reinhardtii*.

FY 2009 Publications

1. Berberoglu H, Pilon L, Melis A (2008) Radiation characteristics of *Chlamydomonas reinhardtii* CC125 and its truncated chlorophyll antenna transformants *tla1*, *tlaX*, and *tla1-CW*⁺. Intl J Hydrogen Energy 33: 6467-6483.
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II.1.3 Biological Systems for Hydrogen Photoproduction

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Project Start Date: October 1, 2000
Project End Date: Project continuation and
direction determined annually by DOE

Objectives

- Engineer an [FeFe]-hydrogenase that has an extended half-life following exposure to O₂, as part of an aerobic algal H₂-production system being developed with other Hydrogen Program-sponsored groups.
- Optimize and use a platform for testing algal mutants with improved H₂-production properties and higher light-conversion efficiencies.
- Address individual components of an innovative H₂-production system based on integrating fermentative and photosynthetic H₂-producing organisms.

Technical Barriers

This project addresses the following technical barriers from the Production section of the Hydrogen, Fuel Cells and Infrastructure Technologies (HFCIT) Program Multi-Year Research, Development and Demonstration Plan (MYRDDP):

- (AI) Continuity of Photoproduction by Green Algae
- (AT) Feedstock Cost in an Integrated System

Technical Targets

The technical targets for this project are listed in Table 1.

TABLE 1. Photolytic Biological Hydrogen Production from Water

Characteristics	Units	2003 Status	2009 Status	2013 Target	2018 Target
Duration of Continuous Photoproduction	Time units	N/A	180 days (-S, anaerobic) 6 days (-S, aerobic, immobilized)	30 min (aerobic)	4 h
O ₂ Tolerance (half-life in air)	Time units	1 s	4 min (clostridial enzyme)	10 min (aerobic)	2 h

N/A - not applicable

Accomplishments

- Demonstrated that purified [FeFe]-hydrogenases show different sensitivity to O₂ inactivation, depending on the presence or absence of reductant during the purification procedure.
- Designed deoxyribonucleic acid (DNA) constructs for expression of recombinant [FeFe]-hydrogenases in *E. coli* upon anaerobic induction; integrated these constructs into appropriate vectors; successfully expressed recombinant hydrogenase in *E. coli* using these vectors; and designed a high-throughput chemochromic assay for screening random mutagenesis libraries for O₂-tolerant hydrogenases.
- Designed a DNA construct for expression of the clostridial, more O₂-tolerant [FeFe]-hydrogenase in the green alga *Chlamydomonas reinhardtii*; demonstrated expression of the gene by reverse transcription polymerase chain reaction (RT-PCR).
- Demonstrated 30-45% higher H₂-gas production by an ATPase mutant (where electron transport is not limited by the formation of a proton gradient) compared with the parental strain, using the sulfur-deprivation, alginate-immobilized platform.
- Showed higher and sustained rates of H₂ production by a sulfur-deprived, truncated-antenna mutant, immobilized in alginate at 1/10th sun, when compared with the parental strain.
- Demonstrated H₂ production by fermentative organisms using starch-rich potato waste, accompanied by production of organic acids; showed H₂ production by photosynthetic bacteria using organic acids from the fermentation of potato wastes.

Introduction

Green algae can photoproduce H_2 using water as the source of electrons. This property requires the coordinated operation of the photosynthetic apparatus (splits water, producing O_2 , electrons, and protons) and [FeFe]-hydrogenases (recombines protons and electrons, producing H_2 gas). The catalytic center of [FeFe]-hydrogenases is composed of a unique 2Fe2S metallocenter that is sensitive to O_2 , a by-product of photosynthetic water oxidation. This inactivation prevents sustained H_2 production by the organism in the light. The continuity of H_2 photoproduction is one of the major technical barriers to developing photobiological H_2 -production systems, as listed in the HFCIT Program MYRDDP (Barrier AI).

Our current project addresses (a) the O_2 sensitivity of H_2 -producing algae by using molecular engineering (both site-directed and random mutagenesis) to alleviate this effect; (b) the further development of a platform, based on the induction of H_2 production by sulfur deprivation, to test biochemical and reactor engineering factors required to improve the rates and light-conversion efficiencies of algal H_2 -photoproduction; and (c) the performance of different components of a proposed system that integrates fermentative with photobiological processes for more cost-effective, biological H_2 production. The latter addresses the MYRDDP Barrier AT (feedstock cost in an integrated system).

Approach

Task 1. Molecular Engineering of [FeFe]-Hydrogenases

This task has two objectives: (a) the engineering of increased O_2 tolerance in [FeFe]-hydrogenase through selective, random mutagenesis of region(s) that control O_2 access to the catalytic site; and (b) the functional expression of clostridial [FeFe]-hydrogenases in *Chlamydomonas reinhardtii*. The efforts being conducted under the first objective have been guided by an extensive computational study of gas diffusion in the clostridial CpI [FeFe]-hydrogenase, which identified four amino acids that form a “barrier” for O_2 migration into the catalytic site. The current experimental strategy is to increase the energy required for O_2 to migrate through this barrier by changing its amino acid composition. A random approach, though more labor- and time-intensive, will create a more comprehensive library of mutants, increasing the likelihood of finding one with improved tolerance. The efforts being conducted under the second objective involve the design of a genetic construct for expression, activation, and translocation of a clostridial [FeFe]-hydrogenase into the stromal

compartment of the algal chloroplast. Clostridial [FeFe]-hydrogenases are ~100x more O_2 tolerant than algal hydrogenases, yet both undergo the same activation process. The progress made through this approach will lead to the development of expression constructs and techniques that will be essential to expressing engineered [FeFe]-hydrogenases in *C. reinhardtii*, and will provide data on the effects of a more O_2 -tolerant enzyme on the kinetics and metabolism of photo-hydrogen production.

Task 2. Optimization of the Sulfur-Deprivation Platform to Test the Performance of Various Algal Mutants

With our collaborators at University of California, Berkeley (UCB), we developed a method, based on depriving algal cultures of sulfate, to induce continuous H_2 photoproduction. This procedure has become a platform for testing the performance of a variety of algal mutants, as well as to study process engineering parameters that affect the light-conversion efficiency of the system. These will become important once an O_2 -tolerant hydrogenase system (see Task 1) becomes available.

Task 3. An Integrated Biological H_2 -Production System

The HFCIT Hydrogen Biological Production working group identified a novel system for biological H_2 production that depends on the coordinated activity of photosynthetic (oxygenic and non-oxygenic) and fermentative organisms. An integrated system has the potential for circumventing the shortcomings of each of the individual H_2 -producing components in terms of limitations in their overall light-conversion efficiencies and substrate dependence. The particular configuration being pursued at NREL involves stacked reactors of sulfur-deprived green algae and photosynthetic bacteria that produce H_2 in the light. The fermentative component consists of anaerobic bacteria that degrade the algal and photosynthetic bacteria biomass and produce H_2 and acetate as products. The latter is the source of reductant for H_2 production by the photosynthetic bacteria.

Results

Task 1. Molecular Engineering of [FeFe]-Hydrogenases

Our initial approach to engineer an O_2 -tolerant [FeFe]-hydrogenase focused on *site-directed mutagenesis* of the amino acids that comprise a single barrier region controlling O_2 access from the hydrogenase's central cavity to its catalytic site. One mutation of this region in the clostridial Ca1 [FeFe]-hydrogenase possessed high O_2 tolerance when expressed and purified from *E. coli* in the absence of reducing agents. However, this property

was also found to be shared by the wild-type enzyme when purified under similar conditions, suggesting that gas accessibility alone may not be the sole determinant of O₂ sensitivity in [FeFe]-hydrogenases. The ability of the enzyme to transition between redox states may also be critical. Moreover, mutations of barrier residues may affect this property as well as gas accessibility. It is possible that this redox effect is similar to one previously described for the “inactive, O₂-resistant” state of the periplasmic [FeFe]-hydrogenases from *Desulfovibrio*, and until now a property known only to those [FeFe]-hydrogenases.

In order to increase the probability of generating O₂-tolerant hydrogenase mutants, we initiated a *random mutagenesis*/high-throughput (HTP) screening approach. It involves the design of expression vectors that can be used in combination with a gas-chromatography-based HTP assay. Work is being performed under subcontract to Golden BioEnergy.

Current site-directed and random mutagenesis efforts were performed with the Ca1 hydrogenase protein, which has a higher tolerance to O₂ inactivation in vitro than either of the two *C. reinhardtii* hydrogenases. To determine how this higher O₂-tolerance affects activity when coupled to algal photosynthesis, we developed a transformation vector to introduce the Ca1 hydrogenase gene into the *C. reinhardtii* genome in a manner that is intended to result in the expression of an active hydrogenase. We completed the transformation of the Ca1 gene into the *C. reinhardtii* strain CC-849 genome and identified by PCR approximately 15 transformants that show the presence of the entire Ca1 codon-optimized gene. The presence of the Ca1 ribonucleic acid transcript was demonstrated by RT-PCR in two transformants, and one of these appears to be anaerobically regulated (as is the case for the endogenous *HydA1* gene). In addition, preliminary biochemical evidence was obtained that suggests one *C. reinhardtii* transformant is expressing the codon-optimized Ca1 [FeFe]-hydrogenase protein. Future efforts will be directed at confirming expression of the Ca1 [FeFe]-hydrogenase protein. In addition, preliminary O₂-sensitivity results will be confirmed and physiological analyses will be pursued.

Task 2. Optimization of the Sulfur-Deprivation Platform to Test the Performance of Various Algal Mutants

Our major accomplishments on this task this past year were: (a) the demonstration of higher sustained rates of H₂ production at low light intensity (1/10th sun) by a truncated antenna mutant, following sulfur-deprivation and immobilization into alginate films; and (b) further confirmation that leaky ATPase mutants, which cannot accumulate a proton gradient across the thylakoid membrane, produce 30-45% more H₂ than the

parental strain at high light intensities. These two results strengthen the hypotheses that H₂ production saturates at low light intensity due to (a) the presence of a large light-harvesting antenna; and (b) down-regulation of electron transport as a proton gradient accumulates across the thylakoid membrane. Our results also suggest genetic approaches to circumvent these limitations.

Task 3. An Integrated Biological H₂-Production System

We completed a series of small-scale batch experiments exploring the ability of a consortium to catabolize algal biomass and pure cellular components for H₂ production. The work demonstrated that the consortium is able to utilize both fresh and frozen (potentially damaged) biomass preparations, as well as biomass from algae that were cultured either in the presence or absence of sulfate (see Task 2). The molar yield of algal biomass fermentation varied from 6.24 H₂/glucose (when the algae were cultured under sulfur-replete conditions) to 0.94-2.30 H₂/glucose (when the algae were sulfur-deprived for different periods of time). The high molar yields of H₂/glucose observed with sulfur-replete algae suggest that the consortium is utilizing biomass components other than starch. In fact, we have demonstrated that the consortium is able to metabolize pure lipid (digalactosyl diacylglycerol) at molar ratios of 0.11 H₂/lipid and pure protein (generic bovine serum albumin) at 0.054 μmol H₂/mg protein, while co-producing organic acids.

Our collaborators in Russia successfully demonstrate H₂ production, concomitant with organic acid production by fermentative organisms using starch-rich potato wastes, and showed that the resulting organic acids were capable of being utilized by photosynthetic bacteria for additional H₂ generation.

Conclusions and Future Directions

Task 1: (a) Further investigate the biochemical properties of purified, wild-type [FeFe]-hydrogenase Ca1 to determine the inactivation kinetics of the O₂-insensitive state(s), the effects of CO, and the effects of H₂ on O₂ sensitivity; (b) characterize the biochemical and gene expression properties of *C. reinhardtii* transformants harboring the Ca1 expression construct; and (c) finish the design and start testing a new gene expression/HTP screen for generating and isolating desired O₂-tolerant hydrogenases.

Task 2: (a) Initiate a new collaboration with Johns Hopkins University to further investigate the properties of the ATPase mutants and exploit them for more efficient H₂ production; (b) test more advanced truncated antenna mutants from UCB; and (c) continue to improve the physical stability of alginate films.

Task 3: (a) Test whether the fermentative consortium can also metabolize photosynthetic bacterial biomass and alginate; (b) scale up fermentation of algal biomass; and (c) continue to optimize photosynthetic bacterial H₂ photoproduction using dilute fermentation products (organic acids) as feedstocks.

Special Recognitions & Awards/Patents Issued

Awarded travel funds by a Brazilian research funding agency (CNPq) to consult with members of the University of Bahia (Ghirardi).

FY 2009 Publications/Presentations

Publications

1. Turner, J, G Sverdrup, MK Mann, PC Maness, B Koproski, ML Ghirardi, RJ Evans, and D Blake. **2008.** *Int. J. Hydrogen Energy*, 32, 279-407.
2. Seibert, M., P. King, M.C. Posewitz, A. Melis, and M.L. Ghirardi. **2008.** *In Bioenergy* (J. Wall, C. Harwood, and A. Demain, Eds.) ASM Press, Washington, D.C., pp. 273-291.
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Presentations

Invited presentations at the Energia de Portugal in Lisbon, Portugal (Ghirardi); International *Chlamydomonas* meeting in Hyeres, France (Ghirardi and Seibert); Gordon-Kenan Graduate Research Seminar at Mt. Holyoke, MA (English); Session chair – hydrogenases, GRC on Iron sulfur enzymes (King); Sustainable Energy Education Training (SEET) session, Golden, CO, July 2008 (Ghirardi); session chair at the Golden Research Conference on FeS enzymes, July 2008 (King); session chairs at the US AFOSR Biofuels Review, Arlington, VA, August 2008 (Seibert and Ghirardi); advisory board member for a University of Tennessee NSF-funded project (Ghirardi); Microbial Genomics meeting in Lake Arrowhead, CA, September 2008 (Ghirardi); co-organizer of an NREL Strategic Initiative Workshop on Novel Materials Synthesis for Renewable Energy Applications, Golden, CO, September 2008 (King); University of Wisconsin, Madison, September 2008 (Seibert); NREL Algal Group monthly meeting at NREL, October 2008 (Ghirardi); International Photosynthesis Conference in Indore, India, November 2008 (Seibert); presentation at the School of Life Sciences, Jawaharlal Nehru University, November 2008 (Seibert); session chair at the Co-Products at DOE's Bioalgal Fuels in Bethesda, MD, December 2008 (Ghirardi; Seibert also attended); the Joint U.S. AFOSR-NREL Biofuels meeting in Golden, CO, January 2009 (Seibert; Ghirardi also attended); Western Regional Photosynthesis conference in Asilomar, CA, January 2009 (Ghirardi); Gordon Conference on Solar Fuels in Ventura, CA, February 2009 (Ghirardi); CSIC, Zaragoza, Spain, April 2009 (Seibert); GLBRC Hydrogenase Forum, May 2009 (Seibert).

NREL visitors: Dr. Steven Chu (Director of the LBL); University of Wyoming professors; Andrew Gillette (Foundation for Computer Learning); Dr. Kevin Redding (Arizona State University); Jonathan Trent (NASA), Drs. Niels van der Lelie and Safiyh Taghavi (BNL), Dr. Plamen Atanassov (Director of the UNM Center for Emerging Energy Technologies); Dr. Patrice Hamel (Ohio State University); Savannah River National Lab researchers; Jacques Beaudry-Losique (DOE's EERE); Prof. Harris (Georgia Institute of Technology); Drs. Andrew Hsu and Kyle Cline (Richard G. Lugar Center for Renewable Energy, Purdue University).

II.1.4 Fermentation and Electrohydrogenic Approaches to Hydrogen Production

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Start Date: October 1, 2004

Projected End Date: Project continuation and
direction determined annually by DOE

Technical Targets

Progress Toward Meeting DOE Technical Targets in Dark Fermentation

Characteristics	Units	2013 Target	2009 Status
Yield of H ₂ from Glucose	mole H ₂ /mole glucose	4	9.95
Feedstock Cost	cents/lb glucose	10	12

- Yield of H₂ from glucose: DOE has a 2013 target of an H₂ molar yield of 4 using glucose as the feedstock. In Fiscal Year 2009 we achieved a molar yield of 9.95 from glucose (derived from cellobiose) by integrating fermentation (H₂ molar yield 1.64) with microbial electrolysis cell (MEC) (H₂ molar yield 8.31) reactor.
- Feedstock cost: The DOE Biomass Program is conducting research to meet its 2013 target of 10 cents/lb biomass-derived glucose. NREL's approach is to use cellulytic microbes to ferment cellulose and hemicellulose directly, which will result in lower feedstock costs.

Objectives

- Perform hydrogen fermentation using cellulytic bacteria and lignocellulosic biomass to lower feedstock cost.
- Perform metabolic pathway engineering to improve hydrogen molar yield via fermentation.
- Develop microbial electrolysis cell to improve hydrogen molar yield using waste from the fermentation of lignocellulosic biomass.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section (3.1.4) of the Hydrogen, Fuel Cells & Infrastructure Technologies (HFCIT) Program Multi-Year Research, Development and Demonstration Plan:

(AR) H₂ Molar Yield

(AS) Waste Acid Accumulation

(AT) Feedstock Cost

Accomplishments

- Performed scale-up bioreactor experiments using the cellulose-degrading bacterium *Clostridium thermocellum* 27405 fermenting various amounts of lignocellulose prepared from the acid hydrolysis of corn stover biomass.
- Demonstrated that when competing metabolic pathways were selectively blocked with the inhibitor 4-methyl pyroazole, output of hydrogen was improved by up to 28%.
- Observed hydrogen production from an MEC reaction using real waste effluent from NREL's lignocellulosic fermentation. When integrated, the two-stage process combining fermentation and electrogenesis produced an overall molar yield of 9.95 mol H₂ per mol hexose, using cellobiose as the substrate.

Introduction

Biomass-derived glucose feedstock is a major operating cost driver for economic hydrogen production via fermentation. The DOE HFCIT Program is taking advantage of the DOE Biomass Program's investment in developing inexpensive glucose from biomass to

meet its cost target of 8 cents/lb by 2015. Meanwhile, one alternative and valid approach to addressing the glucose feedstock technical barrier (AT) is to use certain cellulose-degrading microbes that can ferment cellulose directly for hydrogen production. One such example is the cellulose-degrading bacterium *Clostridium thermocellum* 27405 (*C. thermocellum*), which was reported to exhibit the highest growth rate using crystalline cellulose [1]. Another technical barrier to fermentation is the relatively low molar yield of hydrogen from glucose (mol H₂/mol sugar; Technical Barrier AR), which results from the simultaneous production of waste organic acids and solvents. Biological pathways maximally yield 4 mole of H₂ per 1 mole of glucose (the biological maximum) [2]. However, most laboratories have reported a molar yield of 2 or less [3,4]. Molecular engineering to block competing pathways is a viable option toward improving H₂ molar yield. This strategy had resulted in improved hydrogen molar yield in *Enterobacter aerogenes* [5].

A promising parallel approach to move past the biological fermentation limit has been developed by a team of scientists led by Bruce Logan at Pennsylvania State University (PSU). In the absence of O₂, and by adding a slight amount of negative potential (-250 mV) to the circuit, Logan's group has produced H₂ from acetate (a fermentation byproduct) at a molar yield of 2.9-3.8 (versus a theoretical maximum of 4) in a modified microbial fuel cell (MFC) called an MEC [6]. It demonstrates for the first time a potential route for producing 8 or more mole of H₂ per mole glucose when coupled to a dark fermentation process. Combining fermentation with MEC could therefore address Technical Barriers AR and AS (waste acid accumulation) and improve the techno-economic feasibility of hydrogen production via fermentation.

Approach

NREL's approach to addressing feedstock cost is to optimize the performance of the cellulose-degrading bacterium *C. thermocellum*. To achieve this goal, we are testing various amounts of cellulosic substrates and optimizing reactor parameters to improve longevity, yield, and rate of H₂ production. We are selectively blocking competing metabolic pathways in this organism via chemical inhibitor and testing its effects on H₂ production. The outcome will serve as a proof of concept for the genetic engineering approach. Via a subcontract, PSU is testing the performance of an MEC using both a synthetic effluent and the real waste stream from lignocellulosic fermentation generated at NREL.

Results

Lignocellulose Fermentation

We performed biomass fermentation in scale-up bioreactors with automated temperature (50°C or 55°C), pH (7.0), and pressure controls. The bioreactor was bubbled with nitrogen (N₂) gas (10 cc/min) to allow real-time sampling of H₂ and carbon dioxide (CO₂) via an online gas chromatograph. *C. thermocellum*, previously cultured in crystalline avicel cellulose, was inoculated into a 1.5 L (working volume) bioreactor fed with various amounts of lignocellulose from the dilute-acid hydrolysis of corn stover. Table 1 summarizes rates and molar yields of H₂ production during a period of 90 hours, using corn stover lignocellulose, avicel cellulose and cellobiose (14.6 mM glucose) and lignocellulose (0.56% (w/v); or 20.4 mM glucose) is 86% and 74.5%, respectively. Calculation of the carbon mass balance did not account for those carbon substrates assimilated into bacterial cell mass. Typical compounds found in the fermentation waste are: acetic, formic, lactic, succinic acids, and ethanol, which are ideal substrates for the MEC reaction.

TABLE 1. Effect of substrate loading and temperature on rates and yields of hydrogen in *Clostridium thermocellum*.

Substrate	Hexose, mM	Temperature (°C)	L H ₂ /L/Day	H ₂ Molar Yield
Cellobiose (0.25%)	14.6	55	2.94	1.1
Cellobiose (0.25%)	14.6	50	1.65	1.64
Avicel (0.5%)	30.9	50	1.44	1.51
Corn Stover (0.25%)	9.1	50	0.25	1.67
Corn Stover (0.56%)	20.4	55	0.55	1.33
Corn Stover (0.83%)	30.9	55	1.21	Not determined

Metabolic Engineering

The ultimate goal of this approach is to develop tools to inactivate genes encoding competing metabolic pathways, thus providing more cellular flux to improve H₂ molar yield. To test our hypothesis, we determined effects of metabolic pathway inhibitor on H₂ production. We chose the inhibitor 4-methyl pyrazole, which blocks two reactions: the synthesis of lactate from pyruvate and the synthesis of ethanol from acetaldehyde [7]. The metabolic pathways of *C. thermocellum* clearly suggest that blocking both pathways could potentially conserve more (reduced) nicotinamide adenine dinucleotide (NADH), an ideal substrate for H₂ production (Figure 1). When 3 mM of 4-methyl pyrazole was added to *C. thermocellum* cultured in cellobiose, we detected

FIGURE 1. Cellulose metabolic pathway in *Clostridium thermocellum*. NAD(H): (reduced) nicotinamide adenine dinucleotide; ATP: adenosine triphosphate; ADP: adenosine diphosphate; Fd(H₂): (reduced) ferredoxin

FIGURE 2. Total H₂ production and hydrogenase activity upon the addition of 3 mM 4-methyl pyrazole (4-MP) to a *C. thermocellum* culture fermenting cellobiose. MV: methyl viologen. Rates for MV assay should be divided by 10 to reflect real values.

approximately a 28% increase of H₂ in the culture gas phase (Figure 2). However, the inhibitor did not change the hydrogenase activity measured by H₂ production coupled to reduced methyl viologen. Consequently, the inhibitor study provides the strategy to guide the most efficient genetic engineering effort while serving as proof of concept that the metabolic engineering strategy is scientifically sound.

One criterion for metabolic engineering is to optimize colony formation protocol of *C. thermocellum* on solid agar plate. By lowering the agar concentration from 1.5% (w/v) to 0.7% (w/v), we improved the colony formation by more than 1,000-fold, a significant accomplishment. Using the pIKM1 plasmid (provided by Dr. Wiegel, University of Georgia) which harbors a heat-resistant antibiotic marker (lincomycin), work is

FIGURE 3. Effects of different compositions of selected sources and acclimation procedures on product gas production and composition (hydrogen, methane, and carbon dioxide) for synthetic wastewater (non-accl = not acclimated to individual substrates; accl = acclimated to individual substrates) and fermentation effluents based on cellobiose, two corn stover effluents, and a diluted corn stover.

underway to develop a genetic transformation protocol in this organism.

Microbial Electrolysis Cell

The lignocellulose and cellobiose fermentation effluents provided by NREL consisted primarily of: acetic, lactic, succinic, formic acids, and ethanol. Using just a synthetic fermentation effluent (a mixture of these five compounds) in an MEC enriched to this mixture, the MEC produced an additional 800 ± 290 mL H₂/g chemical oxygen demand (COD) above that produced by the fermentation reactor (mixed inocula tests, or MI). In order to increase hydrogen yields from the fermentation effluent, we devised a procedure to acclimate the bacteria used in the MEC to individual substrates. Using this mixture of bacteria pre-acclimated to the individual compounds, we increased the hydrogen production in the MECs to 980 ± 110 mL H₂/g COD (single substrate inocula tests, or SSI) (Figure 3). Hydrogen yields and production rates with SSI and the synthetic and actual fermentation effluents were 980 ± 110 mL/g-COD and 1.11 ± 0.13 L/L-d (synthetic); 900 ± 140 mL/g-COD and 0.96 ± 0.16 L/L-d (cellobiose); and 750 ± 180 mL/g-COD and 1.00 ± 0.19 L/L-d (lignocellulose). A maximum hydrogen production rate of 1.11 ± 0.13 L H₂/L reactor/d was produced with the synthetic effluent. Energy efficiencies based on electricity needed for the MEC using SSI were $270 \pm 20\%$ for the synthetic effluent, $230 \pm 50\%$ for lignocellulose effluent and $220 \pm 30\%$ for the cellobiose effluent. COD removals were ~90% for the synthetic effluents, and 70% to 85% based on volatile fatty acid removal (65% COD removal) with the cellobiose and lignocellulose effluent. The overall hydrogen yield combining MEC with fermentation was 9.95 mol-H₂/mol-glucose for the cellobiose. These results

show that preacclimation of MFCs to single substrates improved performance, and that we could obtain very high hydrogen yields with this integrated system.

Conclusions and Future Direction

- Using lignocellulose as the substrate and a sequenced strain of *C. thermocellum*, low substrate loading gives rise to higher H₂ molar yield while high substrate loading yields faster rate of H₂ production.
- Blocking competing pathways improves yields of H₂ production.
- The MEC process can produce H₂ both from a real waste effluent from lignocellulose fermentation and a synthetic solution having the same composition as the former.

In the future, we will continue to vary substrate loading to determine its effect on rates and yields of H₂. We will develop tools for molecular engineering in *C. thermocellum*. In the MEC area, we will test different methods of reducing methane production in MEC, operating in continuous mode, using fermentation effluent from NREL.

FY 2009 Publications/Presentations

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II.1.5 Hydrogen from Water in a Novel Recombinant O₂-Tolerant Cyanobacterial System

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Project Start Date: May 1, 2005
Project End Date: Project continuation and
direction determined annually by DOE

Objectives

Develop an O₂-tolerant cyanobacterial system for sustained and continuous light-driven H₂-production from water.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section (3.1.4) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (AH) Rate of Hydrogen Production
- (AI) Continuity of Photoproduction

Technical Targets

Characteristics	Current Status	2011 Target	2018 Target
Duration of continuous H ₂ photoproduction in air	Zero to 30 seconds in air	Produce a cyanobacterial recombinant evolving H ₂ through an O ₂ -tolerant hydrogenase	H ₂ production in air for 30 min

Accomplishments

JCVI

- We have knocked out the native hydrogenase (Hox) in cyanobacterium *Synechococcus* 7942. This knockout mutant has been used as a recipient for transferring O₂-tolerant hydrogenases.
- We have purified *Thiocapsa* O₂-tolerant NiFe-hydrogenase from *Thiocapsa roseopersicina*. Polyclonal antibodies specific for this hydrogenase have been raised and used to verify heterologous hydrogenase expression.
- We established two efficient systems for transferring foreign hydrogenase genes into the cyanobacterial recipient. We have transferred totally nine structural and accessory genes of *Thiocapsa* hydrogenase into the recipient through homologous deoxyribonucleic acid (DNA) recombination. Hydrogenase expression in the host has been verified.
- Our study reveals that the novel environmental hydrogenase shares similar maturation mechanisms to those of *Thiocapsa* O₂-tolerant hydrogenase.
- We have searched global ocean sampling (GOS) metagenomic data for novel hydrogenases. One novel hydrogenase has been cloned from environmental DNAs and heterologously expressed in *T. roseopersicina*. The hetero-expressed hydrogenase is active and is highly O₂-stable. This represents the first report of identifying a novel O₂-tolerant NiFe-hydrogenase from environmental microbes through a metagenomic approach.

NREL

- We cloned the O₂-tolerant *Rubrivivax* hydrogenase genes in two plasmids suitable for expression in *Synechocystis*. One plasmid will integrate *Rubrivivax* genes into the genome of *Synechocystis* via the homologous recombination mechanism.

Genes cloned into the second plasmid will be expressed off plasmid. Expression from both plasmids is driven by a native promoter in *Synechocystis*.

- We generated antibodies and tested their specificity against the various subunits of the *Rubrivivax* hydrogenase. We have verified the transformation of four genes and the expression of two hydrogenase structural subunits.

Introduction

Photobiological processes are attractive routes to renewable H_2 production. With the input of solar energy, photosynthetic microbes such as cyanobacteria and green algae carry out oxygenic photosynthesis, extracting energy from water oxidation. The resulting energy can couple to a hydrogenase system yielding H_2 . However, one major difficulty is that most hydrogen-evolving hydrogenases are inhibited by O_2 , which is an inherent byproduct of oxygenic photosynthesis. The rate of H_2 production is thus limited. Certain photosynthetic bacteria are reported to have an O_2 -tolerant evolving hydrogenase, yet these microbes do not split water, requiring other more expensive feedstock.

To overcome these difficulties, we propose to construct novel microbial hybrids by genetically transferring an O_2 -tolerant hydrogenase from other bacteria into cyanobacteria. These hybrids will use the photosynthetic machinery of the cyanobacterial hosts to perform the water-oxidation reaction with the input of solar energy, and couple the resulting reducing equivalents to the O_2 -tolerant bacterial hydrogenase, all within the same microbe. This addresses one of the key technological hurdles to cost-effective photobiological production of H_2 , overcoming the sensitivity of the hydrogenase enzyme to O_2 , which limits the production of hydrogen in current algal systems.

Approach

Our goal is to construct a novel microbial hybrid taking advantage of the most desirable properties of both cyanobacteria and other bacteria, to serve as the basis for technology to produce renewable H_2 from water. To achieve this goal, we use the following two approaches. The first approach is to transfer known O_2 -tolerant hydrogenases from anoxygenic photosynthetic bacteria *Thiocapsa* and *Rubrivivax* to cyanobacteria. Since only a very limited number of O_2 -tolerant hydrogenase is available, our second approach is to identify novel O_2 -tolerant hydrogenases from environmental microbial communities and transfer them into cyanobacteria.

Results

Transferring O_2 -Tolerant Hydrogenase Genes from *Thiocapsa* into Cyanobacteria

Our goal for this part of the work is to transfer an O_2 -tolerant NiFe-hydrogenase (Hyn) from *T. roseopersicina* into cyanobacteria. We have knocked out a native hydrogenase (Hox) in cyanobacterium *Synechococcus* 7942. This knockout mutant was confirmed not to contain any hydrogenase activities and used as a recipient for transferring the hydrogenase. We previously reported cloning the structural (*hynS/L*) and accessory genes (*hynD/hupK/hypC1/hypC2*) of this hydrogenase and integrating them into the chromosome of *Synechococcus* through homologous DNA recombination, creating a recombinant cyanobacterial strain Hyn3. In the past year, we established two efficient systems to transfer additional accessory genes into the strain Hyn3. Using an expression vector with a different selection marker and flanking regions, we cloned accessory genes *hypF*, *hypE*, and *hypD*. Through homologous DNA recombination, we integrated these genes into the chromosome of the strain Hyn3 and created a new strain called Hyn4. To verify that Hyn4 is authentic, we prepared its chromosomal DNA and used it as template to perform polymerase chain reaction (PCR). Our results confirmed that *hypD/hypE/hypF* genes were indeed integrated into the chromosomes. We further performed Southern blotting to confirm correct genotype for *hypD/hypE/hypF*. Chromosomal DNA was prepared from Hyn4 (Hyn4-8) and wild type strains and digested with NdeI and HindIII (Figure 1). Plasmid pHyn4 (as positive control) was subjected to parallel digestion. A digoxigenin (DIG)-labeled probe corresponding to the entire *hypE* gene was made by PCR (Figure 1a) and used to hybridize the blot made from digested DNAs. Southern blotting results show presence of the entire 5 kb piece in the strain Hyn4, which was the same size as that of pHyn4 (Figure 1b), indicating the genotype of *hypD*, *hypE*, and *hypF* is accurate. We verified isopropyl β -D-1-thiogalactopyranoside-inducible expression of *Thiocapsa* O_2 -tolerant hydrogenase by Western blotting using hydrogenase-specific antibodies. Overall, we have transferred nine structural and accessory genes of *Thiocapsa* hydrogenase into the cyanobacterium.

Purifying *Thiocapsa* O_2 -Tolerant Hydrogenases from *T. Roseopersicina*

To further quantify its O_2 tolerance and to determine its electron mediator requirements in the cyanobacterial host, *Thiocapsa* hydrogenases needs to be purified from *T. roseopersicina*. We sought to purify the enzyme using column chromatography. A crude extract of *T. roseopersicina* was applied to a diethylaminoethyl

FIGURE 1. Southern blot confirmation of integration of *hypD*, *hypE*, and *hypF* genes of *Thiocapsa* O_2 -tolerant hydrogenase into the cyanobacterial strain Hyn4 (Hyn4-8). Panel A: Restriction endonuclease map of the *hypD/hypE/hypF* gene locus in the strain Hyn4. Digestion of Hyn4's genomic DNA with *NdeI* and *HindIII* should release a 5 kb DNA fragment. A 1 kb DIG-labeled probe was made by PCR and used for Southern blot. PCR primers and genomic location of the probe are indicated. Panel B: Southern blot result of the strain Hyn4 (Hyn4-8). Plasmid pHyn4 and wild type PCC7942 genomic DNA were used as positive and negative controls, respectively. gDNA represents genomic DNA. The size of hybridized band, 5 kb, is indicated.

cellulose column, and the loaded column was then eluted with a linear gradient of 0-0.6 M NaCl (Figure 2a). Screening hydrogenase activity in eluted fractions by hydrogenase activity assay revealed that the *T. roseopersicina* hydrogenase was eluted from the column in the fraction #22 (Figure 2b). The enzyme in this fraction was further purified through Mono-S and Mono-Q columns. We are now ready to use purified enzyme for functional analysis.

Identifying Novel O_2 -Tolerant Hydrogenases from Marine Microbes in the Global Ocean

The goal for this part of the work is to identify novel O_2 -tolerant hydrogenases from the ocean and transfer them into cyanobacteria. JCVI's GOS Expedition generated 6.3 billion bps of non-redundant DNA sequences, from which 6.12 million proteins were predicted. They nearly cover all known prokaryotic protein families and double the number of current proteins and, in addition, revealed 3995 GOS-only clusters that have no homology to known protein families. To take advantage of this huge amount of genomic information, we searched novel hydrogenases through analysis of the metagenomic data.

FIGURE 2. Purification of *Thiocapsa roseopersicina* O_2 -tolerant hydrogenase. Panel A: Chromatography of *Thiocapsa* crude extract. The curve for H_2 evolution activity of eluted fractions was in red; the curve of protein concentration was in black; and NaCl gradient 0-0.6M in green. Panel B: H_2 evolution activity assay Purified *Thiocapsa roseopersicina* O_2 -tolerant hydrogenase. CE: crude extract; Fraction 22: Purified hydrogenase

Totally, we found 76 large subunit and 52 small subunit sequences (Figure 3). The numbers of these sequences were further compared to those of hydrogenase sequences previously published in the public database Genbank (Figure 3). For the large subunit, there were 261 National Center for Biotechnology Information sequences (vs. additional 76 sequences we found); and for the small subunit, there were 234 NCBI sequences (vs. additional 52 sequences we found). These data indicate that the GOS study has made significant contribution to the collection of NiFe-hydrogenases in the database.

FIGURE 3. Comparison of the numbers of JCVI's novel hydrogenase sequences with those published in the public database GenBank. The numbers of JCVI's sequences are labeled as purple; and the numbers of GenBank's sequences are in blue.

We reported cloning of a novel NiFe-hydrogenases homologous to *Thiocapsa* O₂-tolerant hydrogenase from the environmental DNA samples. Genes of this novel hydrogenase (*hynS/L*, *hupH* and *hyaD*) were heterologously expressed in *T. roseopersicina* strain GB112131, a mutant strain with all three native hydrogenases knocked out. We functionally analyzed this heterologously expressed hydrogenase and found it was active with both H₂-evolution and H₂-uptake activities. We tested its oxygen-stability in the air and found it is extremely stable. Our results indicate that *T. roseopersicina* accessory proteins were able to complement environmental accessory proteins. We further compared the maturation machineries between the environmental hydrogenase and *T. roseopersicina* hydrogenases by performing complementation experiments. We introduced the environmental *hyaD* gene into *T. roseopersicina* *hynD* mutant strain DYDG2, in which the native *hynD* gene encoding an endopeptidase was knocked out. Western and hydrogenase assay results demonstrate that *hyaD* can fully restore cleavage and enzyme activities of *Thiocapsa* hydrogenase in the mutant DYDG2, despite the fact that HyaD shares only 37% identity to its *T. roseopersicina* counterpart HynD. Overall, our study reveals that the native endopeptidase and *Thiocapsa* hydrogenases share similar maturation mechanisms.

NREL: Transferring O₂-Tolerant Hydrogenase from *Rubrivivax Gelatinosus* to Cyanobacteria

The goal for this part of the work is to construct a cyanobacterial recombinant harboring the O₂-tolerant hydrogenase from *Rubrivivax gelatinosus*, using *Synechocystis* PCC6803 (S6803) as the model host. We used two plasmid vectors to accomplish this goal. Plasmid pPETE_sigD is provided by Prof. Robert Burnap (Oklahoma State University) that features (1) light-regulated transcription, (2) a spectinomycin antibiotic resistance marker, and (3) neutral site for homologous recombination. Four structural genes *coolXUH* encoding the *Rubrivivax* O₂-tolerant hydrogenase

(Figure 4a) have been successfully amplified and cloned into the pPETE_sigD plasmid by replacing its *sigD* gene (data not shown). A S6803 mutant lacking all of its native hydrogenase subunits (Hox⁻; provided by Prof. Teruo Ogawa) served as the recipient with zero H₂-production background. After transformation, PCR analysis of several transgenic lines indicated the deletion of the *Rubrivivax coolL* gene (encoding hydrogenase small subunit) although the spectinomycin resistance gene *aadA* was integrated into the neutral site of the S6803 genome. Meanwhile we have generated and validated three peptide antibodies (CooH, CooX, and CooU) for detecting *Rubrivivax* protein expression in the above Hox⁻ transgenic lines. As shown in Figure 4b, *Rubrivivax* hydrogenase subunits CooH (catalytic subunit) and CooU (unknown function) were both expressed in two out of four tested LXUH transgenic lines, confirming the integration of both genes into the Hox⁻ genome. Since the transfer of up to 12 genes is likely needed to express a functional *Rubrivivax* hydrogenase, we employed a broad host range plasmid pRL1342 (provided by Prof. Peter Wolk, Michigan State University) to express additional genes. We constructed pRL1342_LA plasmid carrying codon-optimized *Rubrivivax coolL* and *hypA* (hydrogenase maturation) genes. PCR result indicated the successful transformation of both genes in two S6803 recipients, wild type and a mutant lacking the hydrogenase large-subunit (HoxH⁻) (Figure 4c). The latter serves as a zero-background host allowing easy detection of *Rubrivivax* hydrogenase activity.

Conclusions and Future Directions

JCVI: From the JCVI's research, we conclude that environmental microbes have significant potential in carrying new genes or pathways that may improve efficiency of renewable energy production. From GOS sequences we found 76 large subunit and 52 small subunit sequences. We succeed in converting a piece of environmental DNA into a novel functional NiFe-hydrogenase and demonstrating its extraordinary O₂-stability. We studied maturation mechanisms of the hydrogenase, which refines our knowledge on [NiFe] hydrogenase assembly machineries. We also purified *Thiocapsa* O₂-tolerant hydrogenase from *T. roseopersicina*. Furthermore, we transferred two structural and seven accessory genes of this hydrogenase into *Synechococcus* and demonstrated that the *Thiocapsa* hydrogenase was expressed in the host.

NREL: The NREL research confirmed the expression in *Synechocystis* of two genes encoding subunits of the O₂-tolerant hydrogenase from *Rubrivivax*. Moreover, we transformed successfully a *Rubrivivax* hydrogenase maturation gene in *Synechocystis*. We have generated antibodies and verified their specificity to each of the *Rubrivivax*

FIGURE 4. (a) *Rubrivivax* hydrogenase structural genes *coolLXUH* for integration into *Synechocystis*. *PpetE*: a light- and copper-regulated plastocyanin promoter. *aadA*: spectinomycin resistance gene (b) western blot showing expression of *Rubrivivax* CooU and CooH proteins in *Synechocystis* Hox- host transformed with the pPETE_LXUH plasmid. Hox: untransformed control; lanes 1-4: four transgenic lines with two lines (lanes 2 and 3) expressing *Rubrivivax* CooU and CooH proteins. (c) PCR verification of the presence of *Rubrivivax* *hypA* and *coolL* genes in *Synechocystis*. PCR primers encompass a DNA region with an expected 2.1 kb product containing three genes (chloramphenicol resistance gene *CAT*, *coolL*, and *hypA*). lane 1: wild type as negative control; lane 2: pRL1342_LA as positive control; lane 3: molecular weight marker; lanes 4 and 5: wild type and HoxH transformed with pRL1342_LA plasmid.

hydrogenase subunits, which will be used to probe expression of additional subunits in future research.

Future Directions

- Verify hydrogenase functionality of novel environmental and *Thiocalpsa* hydrogenases in oxygen (JCVI).
- Continue to transfer genes of the novel environmental hydrogenase into the cyanobacterium and analyze resulting recombinant cyanobacterial strains (JCVI).
- Continue to transfer more genes of *Thiocalpsa* O₂-tolerant hydrogenase into the cyanobacterium and analyze resulting recombinant cyanobacterial strains (JCVI).
- Optimize conditions and transfer additional hydrogenase structural and maturation genes of *Rubrivivax* to express a functional O₂-tolerant hydrogenase in *Synechocystis* (NREL).

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2. S.J. Williamson, Rusch D.B., Yooseph S., Halpern A.L., Heidelberg K.B., Glass J.I., Andrews-Pfannkoch C., Fadrosch D., Miller C.S., Sutton G., Frazier M., and J.C. Venter. The Sorcerer II Global Ocean Sampling Expedition: metagenomic characterization of viruses within aquatic microbial samples. *PLoS ONE*, **2008**, 23; 3(1):e1456.
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5. M.L. Ghirardi, A. Dubini, J.P. Yu, and P.C. Maness. Photobiological hydrogen-producing systems. *Chemical Society Reviews*. **2009**, 38, 52-61.
6. P.C. Maness, J.P. Yu, C.E. Eckert, and M.L. Ghirardi. "Photobiological hydrogen production – processes and challenges", **2009**, *Microbe* 4: 275-280.
7. Q. Xu orally presented "construct a cyanobacterial recombinant for solar H₂ production" at Synthetic Genomics Inc., Aug. 4th, 2008, San Diego, CA.
8. Q. Xu and P.C. Maness orally presented "Update on JCVI and NREL Joint project", Hydrogen Production Technical Team Biological Hydrogen Production Review Meeting, August 7, 2008.
9. Q. Xu and P.C. Maness. DOE Annual Hydrogen Program Review Meeting, Washington, DC, May 18-21, 2009. Presentation pdp# 18.
10. P.C. Maness. Society for Industrial Microbiology Annual Meeting, August 10-14, 2008. San Diego, CA. Poster "Metabolic engineering of cyanobacterium *Synechocystis* PCC6803 for solar H₂ production".
11. Yu, J.P. and P.C. Maness. 18th Western Photosynthesis Conference. January 8-11, 2009. Pacific Grove, CA. Presented a poster "Expression of an oxygen tolerant evolving hydrogenase in *E. coli* and in the cyanobacterium *Synechocystis* 6803".

II.I.6 Use of Biological Materials and Biologically Inspired Materials for H₂ Catalysis*

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Contract Number: DE-FC36-06GO8606

Project Start Date: August 1, 2006
Project End Date: December 31, 2009

*Congressionally directed project

Objectives

- Optimize the hydrogenase stability and electron transfer.
- Optimize the semiconductor nano-particle catalysis, oxygen scavenging, and electron transfer properties of protein nano-cages.
- Gel/matrix immobilization and composite formulation of nano-materials and hydrogenase.
- Device fabrication for H₂ production.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (AL) Light Utilization Efficiency
- (AM) Rate of Hydrogen Production
- (AN) Hydrogen Re-oxidation
- (AP) Systems Engineering

Technical Targets

Photoelectrochemical Hydrogen Production

Protein-Based Hydrogen Production Materials/Devices:

- This project is conducting fundamental studies of hydrogenase enzymes and biomimetic nanoparticle mimics and their incorporation into durable materials. Insights gained from these studies will be applied toward the design and synthesis of hydrogen production materials/devices to probe specific metrics for competitive evaluation including:
 - Shelf life of the hydrogen catalyst.
 - Longevity of catalyst under sustained hydrogen production.
 - Thermal stability.

Accomplishments

- Demonstrated that hydrogenase enzymes can be encapsulated within silica gel matrices for enhanced ease of fabrication, without loss of activity, and with some stabilization towards degradation.
- Demonstrated that hydrogen production activity of encapsulated hydrogenases is sensitive to pH.
- Demonstrated that encapsulated hydrogenase materials can be reused and recycled.
- Demonstrated that electroactive gel matrices (polyviologen and viologen doped silica gels) can be manipulated to effect hydrogen production activity.
- Demonstrated efficient hydrogen production with noble metal nanoparticles synthesized using protein cage architectures. Hydrogen production rates are competitive with enzyme catalyzed (hydrogenase) reactions.
- Discovered that hydrogen production can be achieved with pure noble metal and noble metal alloy composite nanoparticles (2009).
- Demonstrated size dependent catalytic efficiency on a range of nanoparticle constrained nanoparticles and demonstrated that nanoparticle size affect catalytic activity (2009).
- Demonstrated thermal stability of both hydrogenase enzymes and synthetic biomimetic catalyst composites up to 90°C with hydrogen production.
- Determined a potential structural basis for the observed enhanced thermal stability observed for the [NiFe]-hydrogenase from *Thiocapsa roseopersicina* (2009).

- Demonstrated sustained hydrogen production for up to 2 hrs (synthetic catalyst) when coupled to light harvesting system, which meets the 2013 target for continuous photoproduction.
- Demonstrated construction of protein cage nanoparticles with integrated Ru(phen)₃ light-harvesting photocatalyst.
- Demonstrated mediator-less light harvesting and electron transfer to protein caged Pt nanoparticles.
- Demonstrated increased O₂ tolerance for hydrogenase enzymes that meet the 2013 target (10 min).
- Demonstrated that the addition of carbon nanotubes can enhance activity of hydrogenase encapsulated in sol gels (2009).
- Demonstrated that sol gel encapsulation of hydrogenases can be optimized with the addition of carbon nanotubes and polyethylene glycol to yield activities equivalent to the maximum activities observed in solution (2009).

Introduction

There is significant interest in the use of hydrogen gas as an alternative fuel for the rapidly evolving hydrogen fuel cell technology. The practicality of the increased use of hydrogen fuel cell technologies is dependent on the ability to produce stores of hydrogen gas in an efficient, economically feasible, and environmentally sound manner. The development of catalysts for the production of hydrogen gas efficiently from a renewable source is of paramount importance.

Biological production of hydrogen is likely to play a key role in the emerging hydrogen economy. In particular, a group of enzymes, hydrogenases (H₂ases), have attracted a great deal of attention because of their ability to efficiently catalyze the reversible reduction of protons to form hydrogen in the absence of Nobel metals. The catalytic site of H₂ases enzymes consists of unique biological metal clusters (Fe or NiFe) stabilized by carbon monoxide and cyanide ligands.

Approach

Using approaches previously described we have optimized the synthesis of biomimetic catalyst systems by encapsulation of reduced metal nanoparticles (Pd, Pt, Fe, Co, and Ni) within engineered protein architectures to mimic the activity and buried active sites of H₂ases enzymes. These materials, along with H₂ases enzymes themselves, have been incorporated into a variety of polymer matrices for efficient hydrogen production and catalyst stabilization.

Overall we are developing composite materials that consist of hydrogen-generating catalytic materials (either hydrogen enzymes or Pd, Pt, Fe, Co, Ni or mixed metal mimics) coupled to photocatalytic materials (for utilization of light energy) or exogenous reducing agents (chemical or electrochemical). These composite materials represent a practical sustainable means of generating hydrogen gas from fully renewable sources. Our most recent efforts have focused on the characterization of H₂ases stability and the further stabilization of H₂ases enzymes to promote increased durability for their use in materials and hydrogen production devices. In addition, using biomimetic approaches enzyme mimics have been synthesized using a range of metal-based nano-materials, including Pt, Pd, Fe₂O₃, Co₃O₄) that mimic the catalytic properties of the enzyme but can be mass produced more readily and have desirable features in the context of durability and oxygen tolerance.

Results

One of the research thrusts is in the area of biomimetic protein cage templating of nanoparticle synthesis. Protein cages provide a scaffold for composite materials synthesis where the spatial arrangement of small molecules (such as light harvesting systems) and encapsulated nanoparticles is optimized for purposes such as light-driven hydrogen production. The long-term goal of using protein assemblies for energy conversion requires that we need to understand the range of chemistries tolerated by the protein and work to enhance the overall stability and fidelity of the synthetic reactions to which we subject them. The second research thrust focuses on hydrogenase enzymes that are highly evolved biological hydrogen production catalysts. Hydrogenase have tremendous promise to be utilized for hydrogen production in living and biomimetic systems. Our work is based mainly in determining the structural basis for stability of those hydrogenases that naturally have enhanced stability and developing mechanisms to be able to treat hydrogenases as heterogeneous catalysis in materials while maintaining their optimal catalytic efficiencies.

1. Removing the electron transfer mediator: direct light harvesting and catalyst turnover.

To improve the effective number of turnovers the photocatalysts can undergo before significant reaction rate decay is observed we have taken a two-pronged approach. First we have designed and constructed a high lux light emitting diode (LED) light source with an average output wavelength of 460 nm. This wavelength is well suited for both the [Ru(bpy)₃]Cl₂ and [Ir(ppy)₂(bpy)]PF₆ light harvesting catalysts we have employed. The use of this light source over others (i.e. Xe lamps) will improve photocatalyst lifetime by

only providing photons near the desired metal to ligand charge transfer energy. Preliminary results indicate that the initial reaction rate may be slightly depressed compared to the Xe lamp, but that the overall production is equivalent in the $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ system and improved in the $[\text{Ir}(\text{ppy})_2(\text{bpy})]\text{PF}_6$ system (Figure 1). We are currently working to make a protein-photosensitizer construct using a genetically modified small heat shock protein (G41C-sHsp) whose introduced internal cysteine is labeled with either $[\text{Ru}(\text{bpy})_3(\text{Iphen})]^{2+}$ or $[\text{Ir}(\text{ppy})_2(\text{Iphen})]^+$, where Iphen is 5-iodoacetamido-1,10-phenanthroline. We have successfully synthesized both photosensitizer constructs and have successfully labeled G41C-sHsp with both sensitizers with the labeling for the ruthenium compound optimized for a single sensitizer per a subunit. Using the ruthenium complex labeled G41C-sHsp we have mineralized Pt^0 inside the protein cage using the conditions we previously published for sHsp. Using this labeled and mineralized protein in a qualitative hydrogen production test resulted in some hydrogen production indicating that the ruthenium complex retains its ability to behave as a photosensitizer for hydrogen production even after

being attached to the protein. This effort will determine the overall efficiency of a mediator-less system with direct electron transfer between light harvesting and H^+ reduction catalyst [Pub. 2]. Cage stabilization and covalent incorporation of light harvesting molecules into protein cage framework.

We have exploited the small heat shock protein (Hsp) from *Methanococcus jannaschii* as a platform for encapsulation of Pt nanoparticle for hydrogen production. To expand the usefulness of this system we have enhanced the chemical and thermal stability of the Hsp protein cage. We have genetically engineered an Hsp mutant, HspE102C, in which the residue 102 is substituted from glutamic acid to cysteine. This cysteine is now available as a chemically-specific reaction site on the protein cage. Since the residue 102 is located around three fold axis of the Hsp, this cysteine residue is expected to be utilized as a site to cross-link three subunits around the axis together so that the cross-linked cage would become more robust. We have conjugated 5-iodoacetamido-1, 10 phenanthroline (I-Phen) on the cysteine 102, followed by coordination of Fe^{2+} with the three Phen around the three fold axis of the cage. The HspE102C cage cross-linked with the $[\text{Fe}(\text{Phen})_3]^{2+}$ complex maintained its original size (~ 13 nm) even after heat treatment at 80°C for 20 min, whereas the “uncross-linked” HspE102C cage aggregated after heating at 65°C for 10 min. This indicates the $[\text{Fe}(\text{Phen})_3]^{2+}$ complex formed between subunits could work as a “linker” among the three subunits and stabilize the cage structure. Furthermore, since $[\text{Fe}(\text{Phen})_3]^{2+}$ complex is structurally similar to well know photosensitizer $[\text{Ru}(\text{Bpy})_3]^{2+}$ and $[\text{Ir}(\text{Bpy})_3]^+$ for H_2 production catalyzed by Pt, it would be possible to impart light harvesting capability and higher stability to the Hsp cage simultaneously by using a iodoacetamido derivative of these photosensitizer as a cross-linker at the 3-fold axis of the HspE102C.

3. Monitoring and controlling particle size growth of Pt nanoparticles.

We have focused on developing more efficient Pt nanoparticle formation within our protein cages. Previously, we constructed genetically modified LiDps and chemically attached metal binding ligands (phenanthroline) to achieve directed Pt nanoparticle formation within LiDps. Now, we have successively monitored Pt ion binding and Pt nanocluster formation individually using mass spectrometry (MS). We have also developed a serial growth method and monitored nanocluster growth using MS and transmission electron microscopy (TEM).

Genetically modified (S138C) LiDps was prepared and incubated with a small amount of Pt ions ($50\text{Pt(II)}/\text{cage}$) overnight. In order to make a Pt seed within LiDps, Pt treated LiDps were reduced with

FIGURE 1. Light source dependent hydrogen production using either an LED or Xe light source with $\text{Ru}(\text{bpy})_3^{2+}$ (bottom) or $\text{Ir}(\text{ppy})_2\text{bpy}^+$ (top) as the light harvesting system in conjunction with cage-Pt nanoparticles.

equivalent amount of NaBH_4 and dialyzed overnight to remove unreacted Pt. Subsequent growth of Pt nanoparticle within LiDps was induced by introducing 100 or 200 Pt(II)/cage with equivalent amount of NaBH_4 at 65°C for 30 min. Reaction products were analyzed by size exclusion chromatography and elution profiles clearly showed co-elution of protein cages and Pt nanoparticle. Electron micrographs of negative stained Pt-mineralized LiDps revealed an intact cage-like structure and distinct particles were observed with additional 200 Pt(II)/cage without staining. To determine the absolute number of Pt atoms of nanoparticles formed within LiDps, we performed noncovalent mass spectrometry analyses of Pt treated samples. MS analyses indicated seeding step (50Pt(II)/cage) induced formation of nanocluster with 37 Pt atoms within LiDps on average. Further high temperature syntheses with additional 100 and 200 Pt(II)/cage produced Pt nanoparticles containing 168 and 202 Pt atoms within LiDps on average. This approach, seeding and subsequent high temperature, can easily apply to other protein cage systems to improve the efficiency of encapsulation of metal nanoparticles.

4. Molecular conjugation and measurement of electron conduction.

A derivative of the transition metal complex $\text{Ru}(\text{bpy})_3^{2+}$ was conjugated to a mutant (G41C) of Hsp. G41C is a genetic construct that presents cysteines on its interior surface. G41C provided a robust nanoplatform that allowed relatively high loading of an isothiocyanate derivative of $\text{Ru}(\text{bpy})_3\text{phen}^{2+}$ (Figure 2a) onto the cage via conjugation to primary amines. The absorbance from the $\text{Ru}(\text{bpy})_3\text{phen}^{2+}$ at 450 nm was prominent in the cage preparations (Figure 2b). The ratio of $\text{Ru}(\text{bpy})_3\text{phen}^{2+}$ to monomeric subunit was estimated as 2.5 based on the ultraviolet-visible (UV-VIS) absorbance and protein content determined by a bicinchoninic acid assay. This translates to 60 $\text{Ru}(\text{bpy})_3\text{phen}^{2+}$ per cage. The functionalized cage appears as intact 12 diameter particles on TEM grids (Figure 2c). It forms films on silicon wafers coated with poly-L-lysine visualized using field emission scanning electron microscopy (Figure 2d). According to particle counts acquired from these images the fractional area coverage is 0.56, which conforms to that expected from the random sequential adsorption (RSA) model (0.55).

The G41C $\text{Ru}(\text{bpy})_3\text{phen}^{2+}$ conjugate was adsorbed to an indium tin oxide (ITO) electrode. We found that an ITO electrode provided the most favorable background for the expected potential range of the $\text{Ru}(\text{bpy})_3\text{phen}^{2+}$ redox couple ($E_o = 1.26$). The red fluorescence from the $\text{Ru}(\text{bpy})_3\text{phen}^{2+}$ was evident in images acquired using epi-fluorescence microscopy (Figure 2e). The red hue appears slightly less intense than that of the conjugate adsorbed to poly-L-lysine coated plastic microtiter plate wells (Figure 2e, inset).

FIGURE 2. Electron transport from a redox couple conjugated to a protein cage. a) $\text{Ru}(\text{bpy})_3\text{phen-SCN}^{2+}$ conjugation agent; b) UV-VIS spectrum of the functionalized protein cage (G41C $\text{Ru}(\text{bpy})_3\text{phen-SCN}^{2+}$); c) TEM image of G41C $\text{Ru}(\text{bpy})_3\text{phen-SCN}^{2+}$ (scale, 12 nm); d) FE SEM image of G41C G2.5 $\text{Ru}(\text{bpy})_3^{2+}$ on poly-L-lysine coated silicon (scale, 12 nm); e) epi-fluorescent image of G41C $\text{Ru}(\text{bpy})_3\text{phen-SCN}^{2+}$ adsorbed to an ITO electrode surface from a drop; green region is the clean ITO surface; inset is an image of G41C $\text{Ru}(\text{bpy})_3\text{phen-SCN}^{2+}$ adsorbed to poly-L-lysine coated plastic well; f) Cyclic voltammogram trace of buffer (black) and ITO electrode with a film of G41C $\text{Ru}(\text{bpy})_3\text{phen-SCN}^{2+}$ (red); inset is detail of the oxidation curve.

This difference in fluorescence perceived by the eye is validated by the difference in the ratios of the red channel to the total luminescence, which is less for the conjugate adsorbed on the ITO surface (1.15) than for the poly-L-lysine coated surface (1.25). Cyclic voltammograms (CVs) were acquired from the adsorbed film (Figure 2f). There were clear differences between the CV of the buffer (100 mM sodium acetate, pH 5.7) and the adsorbed film. Based on the interpretation that the feature in the positive sweep originates from the oxidation current, the area under this feature yields the total electrons transferred from the $\text{Ru}(\text{bpy})_3\text{phen}^{2+}$ conjugated to G41C in the film. The inset shows that this area is actually quite small. Assuming that the adsorbed amount of G41C in the film conforms to the RSA model, this quantity of electrons would be expected to be transferred if only one of the $\text{Ru}(\text{bpy})_3\text{phen}^{2+}$

per cage were in electrical contact with the electrode surface. The height of the oxidation curve expected if electrons from all the $\text{Ru}(\text{bpy})_3^{2+}$ conjugated to the cage in the film were transferred is shown by the vertical bar in the inset.

These results suggest strongly that the Hsp G41C is fairly insulating and that catalytic H_2 production probably requires diffusion of mediator through the protein shell to contact the encapsulated nanoparticle catalyst. The estimate of $\text{Ru}(\text{bpy})_3\text{phen}^{2+}$ in electrical contact with the electrode depends directly on the estimation of the adsorbed surface coverage and thus could be low. Based on the differences in fluorescence from the adsorbed films mentioned above a rough estimate suggests that perhaps the coverage on the ITO electrode is 50% that on the poly-L-lysine coated surfaces. However, the difference between the expected height of the oxidation curve if all electrons from the film were collected, and the actual height, is still striking.

5. Investigation and optimization conditions for developing composite materials based on encapsulation of hydrogenase and multiwall carbon nanotubes into sol-gel.

During the reporting period we have been continuing our work on the optimization conditions for hydrogen production by the *T. roseopersicina* hydrogenase encapsulated into sol-gel. We have shown that hydrogenase encapsulated into sol-gel remains active in presence of carbon nanotubes. The results of these experiments provide the important information about the properties of composite materials composed of silica-gel, carbon nanotubes and encapsulated hydrogenases indicating that carbon nanotubes have high efficiency to conduct electron flow from electron donor/acceptor to hydrogenase in silica-gel. Different type of carbon nanotubes (single- or multi-wall nanotubes) has been developed for this application. The results of our experiments with single- or multi-wall carbon nanotubes show no difference in the activity of hydrogenase encapsulated into sol gel in presence of 4 mM methyl viologen (MV) as an electron carrier.

We have shown previously that increasing the concentration of nanotubes increases the hydrogen production by the hydrogenase in presence of MV. In this study we for the first time are showing the direct transport of electrons through multiwall carbon nanotubes to the hydrogenase without using MV as an electron carrier (Figure 3). Addition of MV increases the hydrogen evolution by encapsulated hydrogenase. The hydrogen production by this system was significantly dependent on the pH of the reaction mixture and was 5 times higher at pH 5.5 in compare to pH 8.0. It has been shown that activity of hydrogenase in solution also dependent on pH and was ~2 times higher at pH 5.5 than at pH 8.0 (Figure 3) [1].

FIGURE 3. Effect of pH and concentration of multi-wall carbon nanotubes on the hydrogen production by encapsulated hydrogenase.

We have examined the effect of the addition of polyethylene glycol (PEG) to gels on the activity of *T. roseopersicina* hydrogenase at different pH. Previously it has been shown that the addition of PEG to sol gels can modulate the pore size of the gels and have significant effects on mass transfer [2]. The reaction mixture consists of 50 mM phosphate buffer pH 5.5, 7.0 and 8.0 and polymerized sol gel. The sol gel was prepared from tetramethoxy silane with the addition of different concentrations of PEG with molecular weight 400 (PEG 400) and/or multiwall nanotubes in presence of 2 or 4 mM methyl viologen. Sol gel was polymerized during 10 min with the addition of an equal volume of 0.8 mg/ml hydrogenase in 50 mM phosphate buffer pH 7.5. The results of our experiments show that increasing PEG concentration from 0% to 20% increases the activity of hydrogenase, whereas 40% PEG inhibited the hydrogen production by encapsulated hydrogenase. The addition of PEG did not influence on the hydrogenase activity in solution. The results of our experiments show that optimum conditions for the development of composite material based on encapsulation of hydrogenase and nanotubes consist of 20% PEG and 2 mg nanotubes and 4 mM methyl viologen at pH 5.5. Under these optimal conditions for encapsulation, hydrogenase activities equivalent to the maximum activities in solution were observed.

6. Structural analysis of the [NiFe]-hydrogenase from *Thiocapsa roseopersicina*.

During the current grant period we have been working on structural characterization of *T.*

roseopersicina [NiFe]-hydrogenase. It has been shown that this hydrogenase is stable to high temperature and oxygen. These properties make this enzyme attractive in the application for hydrogen producing materials. We have previously reported our progress toward the structure of the [NiFe]-hydrogenase from *T. roseopersicina* using cryo electron reconstruction experiments. It has been shown that at high protein concentration (~10 mg/ml) this enzyme forms the supermolecular complex [3]. The specific interactions that stabilize this structure are likely significant to the overall stability of this enzyme and the structure of this assembly is of significant interest in order to identify these factors. We have determined the low resolution structure of hydrogenase assembly using cryo-electron microscopy revealing the supermolecular complex consists of six dimers, organized in D3 hexamer and that the C-terminus of the small subunit of each dimer are involved in key interactions that stabilize the complex. We have also obtained crystals of this hydrogenase and have determined the structure by multiple isomorphous replacement and anomalous scattering methods. Figure 4 shows images of electron density map, obtained after phase extension, using CCP4 program presented in Figure 4. These results correlated with the CryoEM reconstruction images, showing 3-fold (Figure 4 (A, C), 2-fold (Figure 4 C, D) and inner core structure of *T. roseopersicina* hydrogenase supermolecular complex. The secondary structure elements are clearly visible in these maps and we have started to build the structure into these maps taking advantage of the known structure of the [NiFe]-hydrogenase from *D. gigas* as a starting model.

Conclusions and Future Directions

The project has laid a firm groundwork for the use of H₂ases and synthetic mimetics in hydrogen producing materials. The project demonstrates that materials can be generated that have reasonable shelf lives and high catalytic capabilities. We have systematically developed strategies to adapt both H₂ases and synthetic mimetics for use in prototype hydrogen production devices. The salient advancements in the previous year of funding include:

- Major advancements were made in the area of synthesis of noble metal and noble metal alloy catalytic nanoparticles and the incorporation of nanoparticles and H₂ases into electroactive gels and onto surfaces.
- Tools have been developed to advance biomimetic/biohybrid device design and fabrication.
- Twenty two presentations and publications and one patent pending.

The remainder of the project will focus on preparing manuscripts for publication and as future directions we

FIGURE 4. Structural characterization of hydrogenase from *T. roseopersicina*. A, B, C are 4.5 Å MIR phased map, D, F, G Cryo electron microscopy reconstruction model. A and C represented 3-fold symmetry, B and F – 2 fold symmetry, C and G inner core of hexamer structure.

will focus mainly on the direct attachment of catalysts and the attachment of gel encapsulated catalysts to electrode surfaces to directly assess the efficacy of our novel materials for use in devices.

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Patents Issued

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FY 2009 Publications/Presentations

John Peters

Publications

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Trevor Douglas

Publications

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Presentations

1. Astrobiology Center, University of Colorado Boulder, Nov 12, 2008.
2. “Protein Cage Architectures: templates for molecular and materials science” Dec 2008 – Hunter College NY, Department of Chemistry.
3. “Viral Capsids And Other Self-Assembled Protein Cage Architectures: Supramolecular. Templates For Molecular And Materials Encapsulation” February 5, 2009 - Harvard University, Department of Chemistry.
4. “Capsids for synthetic encapsulation: polymers, molecules and nanosolids.” Invited speaker at Gordon Research Conference on Physical Virology, Feb 15–20, 2009, Galveston Texas.
5. “Self-Assembled Protein cage Architectures – Supramolecular Templates for Nanomaterials Synthesis” April 2009 Invited Speaker at 12th International Seminar on Inclusion Compounds, Stellenbosch, South Africa.
6. “Self-Assembled Protein cage Architectures – Supramolecular Templates for Nanomaterials Synthesis” April 2009 – University of Minnesota Department of Chemistry.

II.J.1 Purdue Hydrogen Systems Laboratory: Hydrogen Production*

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Contract Number: DE-FC36-06GO86050

Subcontractor:
National Renewable Energy Laboratory, Golden, CO

Project Start Date: September 16, 2006
Project End Date: September 30, 2010

*Congressionally directed project

Accomplishments

- Issues associated with the feedstock homogeneity were addressed only to a certain extent in the first year using mixing techniques. More recent work addressed these issues more completely by using statistical sampling techniques. Experiments with homogenized distillers grain in addition to food waste are in progress.
- Biomass water content in the first year was relatively high at 98% and is now reduced to as low as 60% with improved material handling and pH control techniques.
- A second solar collector was added to the apparatus this year allowing both biomass waste processing as well as steam generation. The efficiency of the solar collector system for steam generation was measured to be 58%. This capacity addition has decreased the system thermal response time and will allow more detailed estimation of biomass processing efficiency in year three.

Introduction

This project allows the creation of a Hydrogen Research Laboratory in a unique partnership between Purdue University's main campus in West Lafayette and the Calumet campus. This laboratory is engaged in basic research in hydrogen production and storage and has initiated engineering systems research with goals established as per the U.S. DOE Hydrogen, Fuel Cells, and Infrastructure Technologies Program. Hydrogen storage research of this project is reported in report IV.H.1.

Bio-production of hydrogen is potentially an important renewable source of energy. Using organic wastes for bio-production of hydrogen not only has the potential to generate cost-effective and renewable energy but also can reduce pollution in the environment and provide a source of fertilizer for growing crops. The purpose of the current research effort is to investigate, obtain data, and evaluate initial processes for the production of hydrogen from various waste streams using microbial fermentation and investigate possible paths for implementation of the technology as a local electric and thermal energy source. This effort is targeted to assure that the developed technology will be applicable for integration into various current and future energy supply options including the Department of Energy Road Map.

Objectives

Investigate and evaluate initial processes for the production of hydrogen from various waste streams using microbial fermentation and investigate possible paths for implementation of the research in an energy source.

Technical Barriers

This project addresses the following technical barriers from the Production section (3.1.4) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan (Revision 2007):

- (AR) H₂ Molar Yield
- (AT) Feedstock Processing Cost
- (AU) Systems Engineering

Technical Targets

Biological H ₂ Production	Units	2013/2018	Purdue 2009
Hydrogen Yield Percentage	%	33/50	utilizing organic wastes

Approach

We are considering methods to optimize hydrogen production from waste through the use of a fermentation process. The optimization procedure will form the foundation for the subsequent development of a modular device that will use various waste streams, including garbage, animal or human waste, and distillers grain for the production of hydrogen. This hydrogen will be separated from the bio gas stream by use of nano catalyst or a membrane for use in a fuel cell or reciprocating engine to produce electricity locally. Methods to sequester carbon dioxide as part of the process are also being considered. Energy for the pre- and post-processing of feed streams is being obtained from a solar collector system. A steam generator is being added to the solar system for the production of potable water. Computer simulations of the process indicate that the system can be installed in a shipping container and used to provide local electric and thermal energy. Initial efforts have reduced the amount of water in the processed waste material from 98% to 60% with minimal decrease in hydrogen production. By reducing the fraction of water it will be possible to reduce the volume and weight of the bio reactor and increase the system efficiency.

Results

In this study, additional inoculua have been tested and the concentration of hydrogen in the produced gas has been correlated with the experimental variables: pH, temperature, and substrate concentration. Test samples and data are being exchanged between Purdue Calumet and Lafayette and trials to test repeatability are underway. A micro gas chromatograph is used to determine gas composition. Testing to determine operating parameters for hydrogen production from distillers grain is also underway. The testing project is based upon a central composite experimental design. We are currently at the third iteration for the optimization of the hydrogen production levels. This process identifies combinations of operating variables that maximizes hydrogen production. Figure 1 depicts the third generation optimization of hydrogen concentration using the Simplex methodology with an optimum point at 36.9°C, starting pH 6.2 and 1.0 g/25 ml concentration. The multiple testing device is fully operational and is being used to generate data. This device provides the capability to conduct multiple simultaneous tests with automated data processing and monitoring. Continuous production testing is currently being conducted at Purdue Lafayette. Initial approaches to a dry substrate design are being investigated at Purdue Calumet and Lafayette. The model for the modular energy system was updated based upon new experimental values. Efforts using a catalyst process for

FIGURE 1. Mole percent hydrogen produced from fermentation of food waste as a function of temperature and initial pH for 1 g/27 ml concentration.

capture of carbon dioxide have been initiated. Distillers grain has been used to produce hydrogen and matrix tests of operating conditions are starting. During the summer of 2009, the production of potable water from the solar system will be tested; a second bank of collector tubes and a steam generator will be installed.

Conclusions and Future Directions

The biological hydrogen production component of the project has been conducted with a focus on optimizing the microbial fermentation process for hydrogen generation and for preliminary system energy analysis. We have increased the hydrogen production levels by over 50% with current techniques and operating parameters as compared to the prior year. Newly developed techniques have greatly increased both accuracy and precision. Water content has been decreased from 98% to 60% with a small decrease in hydrogen production levels.

We will continue investigating optimal hydrogen production cultures for different substrates, reducing the water content in the substrate, and integrating results from the vacuum tube solar collector pre- and post-processing tests into an enhanced energy system model. The automated testing device developed will be used to further consider optimal hydrogen production conditions using statistical testing procedures. We will also explore existing catalytic methods including nano catalysts for capture of CO₂ from the fermentation process. Next year these optimization efforts will continue and be used to develop a preliminary design and operating procedures for a bench top bio reactor. A conceptual

design for a bench top biological reactor for anaerobic hydrogen production will be developed. Issues considered will include material flow, physical design, thermal control, hydrogen production rates, interface to pre- and post-processing, and operating parameter control. Preliminary issues associated with the design of a commercial prototype modular energy system will also be considered.

FY 2009 Publications/Presentations

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2. Kramer R., "Demonstration of Biological Waste Processing System for Hydrogen Production and Local Energy Production", *Lugar-Visclosky Energy Forum and Expo*, October 2008.

II.J.2 Developing Improved Materials to Support the Hydrogen Economy*

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Contract Number: DE-FC36-04GO14215

Start Date: March 1, 2004

Projected End Date: December 31, 2010

*Congressionally directed project

commercialization. The subject technology must be related to the U.S. Department of Energy hydrogen economy goals as outlined in the multi-year plan titled, "Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan." Preference will be given to cross-cutting materials development projects that lead to the establishment of manufacturing capability and job creation.

Approach

EMTEC has used the U.S. Department of Energy hydrogen economy goals as outlined in the multi-year plan titled, "Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan" to find and fund projects with near-term commercialization potential. Our approach specifies proposals/projects for hydrogen production, hydrogen storage or hydrogen infrastructure processing which may include sensor, separator, compression, maintenance, or delivery technologies. EMTEC is especially alert for projects in the appropriate subject area that have cross-cutting materials technology with near-term manufacturing opportunities. To date, EMTEC has selected projects through our request for proposal process which develop novel technologies preparatory to commercialization. EMTEC's overriding objective is technology commercialization.

Accomplishments

- From project start, EMTEC has funded and provided oversight to over 30 projects in various phases of development.
- EMTEC hosted and attended individual project reviews for the active projects and final site visits for the projects completed throughout the year. EMTEC is continuing site visits for remaining capstone projects.
- EMTEC attended the National Hydrogen Association Conference, March 30 – April 3, 2009.
- EMTEC hosted a half-day short course on April 30, 2009 at the Engineers Club of Dayton, OH. This course was presented by fuel cell expert, Dr. Jack Brouwer of the National Fuel Cell Research Center, University of California, Irvine.
- EMTEC attended and presented a poster at the DOE Hydrogen Program Merit Review, May 18 - 22, 2009.

Objectives

- Foster the investigation and advancement of cross-cutting, breakthrough materials technologies to yield an award-winning program with active DOE Hydrogen Office participation (technology commercialization).
- Manage ongoing hydrogen infrastructure projects; collect and review monthly project reports for Go/No-Go results (near-term commercialization of technologies, products and processes in support of the hydrogen economy).
- Prepare quarterly project reports from individual project reports; negotiate statements of work for selected projects.

Technical Barriers

The projects under this award (this period) address a wide range of barriers from the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan.

Technical Targets

The Edison Materials Technology Center (EMTEC) will solicit and fund hydrogen infrastructure related projects that have a near-term potential for

Conclusions and Future Directions

EMTEC has leveraged DOE initiative and funds on a 1 to 1 match basis on this highly successful project; resulting in strong technology advancement as well as job creation and economic development. Having been successful in years past, EMTEC is evaluating various projects for R&D100 Award submissions.

Future Directions

- Manage and close-out ongoing projects.
- Finalize technical governance site visits with all remaining projects.
- Seek new opportunities to continue technology development and commercialization activities as appropriate for the most promising technologies.

Faraday Technology, Inc.

Project: EFC-H4-1A, Tunable Diode Laser Absorption Spectroscopy (TDLAS) Sensor for In-Line Continuous Monitoring of PEM Fuel Cells & Electrolyzers

Project Objectives

- Design and build of single-cell bipolar plates with simple channels and transparent ports parallel to each channel allowing introduction of the diagnostic laser.
- Redesign/adaptation of the TDLAS for sensing down the length of a channel.
- Demonstration of the TDLAS for moisture or oxygen sensing down the length of a channel in a bipolar plate.
- Conceptual design of a TDLAS capable of continuous, sequenced in-line sensing of a fuel cell or electrolyzer stack.
- Estimation of the capital and operating cost of the TDLAS for in-line fuel cell or electrolyzer stack monitoring.

Accomplishments

- Demonstrate ability of the TDLAS to rapidly respond to moisture changes within the bipolar plate channel, and to monitor the moisture content within the range of 0 to 30,000 ppm.
- Conceptual design of a TDLAS application for continuous in-line sensing of multiple ports in a bipolar plate and stack, including monitoring of the interior channels of a bipolar plate.

Intoduction: There exists a need for close monitoring of the environmental conditions inside the electrolyzer of fuel cell bipolar plates.

Approach: Develop a standoff TDLAS application, where the measurement path is defined by the combination of a transceiver that illuminates and receives light scattered from a diffuse surface or transmitted through a channel. A transceiver unit transmits the laser beam that, like a flashlight, illuminates a distant diffuse surface. The transceiver collects laser light backscattered from the illuminated surface, and concentrates the received laser power onto the photodetector. The photodetector converts the received laser power into an electrical signal transmitted to a signal processor. The standoff TDLAS signal processor analyzes the photodetector's electrical signal to deduce the amount of target gas contained in the laser path (Figure 1).

Results: Figure 2 shows a plot of moisture concentration within the channel as a function of time. During the experiment, moist air, room air and dry air were alternately purged through the channel, and the results monitored using the TDLAS. Figure 2 shows the ability of the TDLAS to rapidly respond to moisture changes within the bipolar plate channel, and to monitor the moisture content within the range of 0 to 30,000 ppm.

Conclusions and Future Directions: Faraday, with input from Physical Sciences, Inc., designed and built a bipolar plate with sensor ports incorporated into the side of the plate, such that the TDLAS sensor was able to measure the moisture content of the channel. Physical Sciences, Inc. redesigned the TDLAS sensor for insertion into the ports incorporated into the bipolar plate. Design considerations included the placement and angle of insertion of the sensor. Faraday and Physical Sciences, Inc. successfully demonstrated the ability to sense moisture in the channel of a bipolar plate using the TDLAS, with moisture contents from 0 to 30,000 ppm. Faraday completed a conceptual design of a TDLAS application for continuous in-line sensing of multiple

FIGURE 1. Anticipated configuration of the GasScan™ TDLAS sensor for in-line diagnostic monitoring of fuel cell and electrolyzer bipolar plates.

FIGURE 2. Sensor response in the current configuration to changes in moisture within the bipolar plate.

ports in a bipolar plate and stack, including monitoring of the interior channels of a bipolar plate.

At this early stage of development, an estimate has been made of approximately \$10,000 for the TDLAS control unit and \$500-1,000 for each measurement port. With future development, these cost estimates may decrease.

Future Directions: Continue exploring refinements of in-situ sensor technologies.

Makel Engineering, Inc.

Project: EFC-H4-15A, Low Cost MEMS Hydrogen Sensor for Transportation Safety

Project Objectives: A low-cost, high performance hydrogen safety sensor for hydrogen-powered vehicles is in development. The proposed system meets a need for a low-cost sensor for on-vehicle safety, pipeline/fueling station monitoring for hydrogen distribution, and has the potential for use in closed-loop fuel cell control loops. In order to meet this emerging market need, Makel Engineering, Inc. (MEI) is adapting our hydrogen sensing technology and integrating recently developed hydrogen-sensitive nanomaterials into a highly manufacturable system platform. A second generation prototype system that will be tested on hydrogen-powered vehicles will be produced.

- Refine nanocluster sensor manufacturing processes for reliable production.
- Develop ultra-low power prototype personal hydrogen sensor system.
- Demonstrate prototype commercial system.

Accomplishments:

Initial prototype layouts have been generated for the ultra-low power circuitry that will allow the system to run for ~1 year without the need to change the battery. The device will incorporate a low-cost microcontroller, which can enter a “sleep” mode up to 99% of the time to conserve power (Figure 1).

Introduction: The use of hydrogen fuel in transportation applications requires the development of compact, reliable, low-cost instrumentation for safe operation and process control. Users and maintainers of these systems require a safety monitoring system, as hydrogen leaks present an explosion risk, especially in early devices as hydrogen containment technology is still being proven.

Approach: Adaptation of MEI’s thin film hydrogen leak detection sensor system originally designed for NASA, for use in automotive applications.

Results: Lower cost, automotive-grade electronics and packaging were designed and are being produced for use in Ford’s demonstration tests. Preliminary investigation of palladium nanocluster sensor elements produced by Argonne National Laboratory was performed by MEI.

Future Directions

- Continue development of “wearable” prototype design.
- Continue laboratory and field testing of low cost prototype sensors.
- Develop plan for additional market entry.

FIGURE 1. Commercially-Available, Keychain-Sized CO Detector (Left); Concept Drawing of Personal Hydrogen Sensor Badge (Right)

Powdermet Inc.

Project: EFC-H4-12, High Strength, Low Cost Microballoons for Hydrogen Storage

Project Objectives

- Working prototype evaporative coating chamber for powders.

- 1 μm Al coating on glass microballoons.
- Varying Al coating on glass microballoons from 100 nm to 2 μm .
- Demonstrate 5,000 psi hydrogen storage in commerciality available glass microballoons.
- Record leak rate of 5,000 psi hydrogen-filled commercially available glass microballoons.
- Coat up to 1 μm Al coating onto 5,000 psi hydrogen filled glass microballoons.
- Record leak rate of coated vs. uncoated hydrogen filled commercial microballoons.
- Vary coating thickness from 100 nm to 2 μm and measure leak rates vs. storage density.
- Produce 5-10 L of microballoon fuel filled at 5,000-8,000 psi.
- Use Microballoons in Phase II prototype hydrogen delivery system to power a fuel cell.

Accomplishments: Demonstrated that high strength coating using chemical vapor deposition (CVD) in a fluidized bed, very thin, high strength coatings (1-20 μm) can be applied to the ultra lightweight (0.05 g/cc) carbon microballoon “scaffolds” in a very cost-effective manner, leaving no residual gas inside the spheres that potentially reduce capacity. In Phase I coatings on microballoons with a thickness of 1-15 μm were deposited.

Introduction/Approach: Powdermet is investigating alternative methods to “lock in” hydrogen to already commercially available high strength glass and silica microballoons for demonstrated use in a prototype delivery device (Figure 1).

FIGURE 1. Prototype Microballoon Delivery Device

Powdermet’s evaporative powder coatings should take advantage of existing glass microballoon’s already high strength ability to store hydrogen and augment its ability to prevent the hydrogen from leaking over time. Existing glass and silicon microballoons have been shown to hold 10% hydrogen by weight, however, hydrogen leaking is a major problem.

Results: Although the first part of Phase II failed to produce large quantities of balloons that held substantial quantities of hydrogen, breakthroughs in microballoon development essential to other Powdermet products were achieved and a prototype delivery device was fabricated. Table 1 shows the potential for these microballoons to be a very effective weight-based storing solution for hydrogen although their volumetric potential is limited certain applications such as aircraft and personal portable power require weight savings over volumetric savings.

TABLE 1. Theoretical Analysis Meeting DOE On-Board Hydrogen Storage Targets

Storage Parameter	Units	DOE 2010 Target	Theoretical Limit Powdermet CVD Coated Carbon Microballoon @ 20,000 psi	Theoretical with Designed 1.5 Safety Factor (practical limit) @ 14,000 psi
Specific Energy	kWh/kg	2	5.49	3.67
Energy Density	kWh/L	1.5	1.32 (Assumes monosized spheres.)	0.84 (Assumes monosized spheres.)

Conclusions and Future Directions: Powdermet can take the state-of-the-art hydrogen-filled glass balloon technology and improve on this by eliminating the hydrogen leaking potential by using nanometer controlled evaporative coatings on the glass microballoons. This technology will enable Powdermet to reach its goal of microballoon hydrogen storage of 10% by weight and augment many other internal Powdermet projects allowing aluminum and other metal deposition on materials at “cold” substrate temperatures without the need for chemical vapor deposition.

Future Directions

- Assembly and operation of evaporative Al system for coating powders.
- Hydrogen storage in glass microballoons and leak rate measurements. Coating hydrogen filled microballoons and leak rate measurements.
- Scale up of process and prototype demonstration.

Precision Energy and Technology (PET)

Project: EFC-H4-23, Supporting Continuous Reel to Reel, High Volume, Low Cost MEA Production with a Continuous Manufacturing of a GDE Anode and Cathode Reel Manufacturing Process to Integrate into the MEA Bonder System

Project Objectives

- Refine a system to continuously manufacture an electrode on a reel system of at least 50 meter length.
- Develop an electrode fabrication method using suitable carbon-carbon-teflon-catalyst (particle-nanofiber-pitch-catalyst-teflon) techniques for improved quality and cost.
- Develop improvements in catalysts blends for better costs and quality of reactions.
- Investigate the use of 3-dimensional catalyst techniques to improve reactions for hydrogen generation.
- Making membrane electrode assemblies (MEAs) more cost-effective and providing the marketplace multiple MEA products at the lowest production cost.

Accomplishments

- Developed reel-to-reel MEA process equipment (Figure 1).
- Developed plan and implement a design of experiments for the best performance versus cost trade-off for a matrix of catalysts types.
- Developed plan and implement a design of experiments for various layering techniques of the catalysts, carbon, and Nafion®.

Introduction: With the Department of Energy's target of \$30 per kilowatt for proton exchange membrane (PEM) fuel cells, considerable work is needed in the high

speed processing of the MEA bonding process. Up to this point, the majority of global MEA production has been by batch processing. In batch processing, all of the sub-component layers, (electrolyte membrane, cathode layer and anode layer) are pre-cut to size then formed into a single layer by a thermal pressing process.

Approach: MEAs are assembled in the bonder system (Figure 1) by continuously feeding a solid PEM style electrolytic film (e.g. DuPont Nafion® 112) from the top left reel and feeding the film down the center of the system. The anode and cathode reels, located on the left and right sides, unwind intermittently and are cut into individual panels that are held in position by pneumatic belts. The timing interval for electrode feed is controlled by the operator's electrode length setting. While platinum continues to be the major player in catalyst reactions, other materials are creeping into the blend. Nickel, cobalt, ruthenium, rhodium, etc. are being considered as part of the opportunities for lowering costs and improving reactions.

Results: Currently, the unit appears capable of producing 1,500 to 2,000 – 50 cm² units per day. At that rate, the MEA Bonder could produce half a million MEAs per year. This unit does have some limitations, though. The original specification required that the electrodes have a minimum of 50 mm to a maximum 150 mm width and a limit of 50 mm to 300 mm length. This does allow for a significant variety in sizes. Initial inquiries were for 6 cm² and 12 cm² area. PET is currently modifying the machine to produce the smaller size MEAs.

A review of the layering techniques in a performance versus costs analysis will provide direction in the manufacturing methods needed to optimize the costs versus performance curve. Evaluations of sputtered and laser ablation of platinum have been observed to produce a significant layer of platinum at .007 mg per cm². While the surface coverage was nearly continuous, the catalyst reaction was not. Additional work with layering the catalyst is showing promise. Some experiments with thin layering of catalyst, carbon, Nafion®, show improvements worth examining.

Conclusions and Future Directions: Much work is still needed to enable high volume manufacturing of MEA that will meet cost and performance targets now and in the future.

Evaluations of sputtered and laser ablation of platinum have been observed to produce a significant layer of platinum at .007 mg per cm². While the surface coverage was nearly continuous, the catalyst reaction was not. Additional work with layering the catalyst is showing promise. Some experiments with thin layering of catalyst, carbon, Nafion®, show improvements worth further examination.

FIGURE 1. PET's MEA Bonder System

Special Recognitions & Awards/Patents Issued

- 1. Provisional Patent Filed: MEA Bonder electrolyte-electrode position control/timing the MEA.**

Technology Management, Inc. (TMI)

Project: EFC-H4-14A, On-Farm Soybean-Powered TMI SOFC System Demonstration

Project Objectives

- Demonstrate a fuel cell system producing 1 kilowatt of electricity operating directly on soybean oil.
- Provide additional engineering data necessary for downstream product development.
- Improve the long-term performance of cell and stack components necessary for the demonstration and downstream products.

Accomplishments

- Site selected for demonstration – installation completed April 2009.
- Ten-cell stack operation on natural gas continuously for 1,400 hours.

Introduction: Under this award, TMI utilized this award to augment work for the demonstration of a fuel cell system producing 1 kilowatt of electricity operating directly on soybean oil being conducted on behalf of the Ohio Soybean Council (OSC). The overall demonstration project continued the commercialization efforts of TMI by advancing prototype system testing at an end-user site in order to provide additional engineering data necessary for downstream product development. TMI will use the Phase III funding to improve the long-term performance of cell and stack components necessary for the demonstration and downstream products.

Approach: Building on knowledge from previous short-term demonstrations (at the 2006 OSC board meeting and the 2007 Farm Science Review), this project tested a TMI solid oxide fuel cell (SOFC) system operating on actual end-user loads providing useful alternating current power for a period of approximately 30 days.

For a successful demonstration, improved stack longevity was demonstrated. Under this project, several advanced electrode materials developed by TMI were evaluate for long-term performance in tests of >1,000 hours. These materials were selected for mechanical stability with chemical stability considerations but were verified to ensure satisfactory long-term performance. A preliminary characterization of the advanced electrode degradation under several operating conditions was conducted. A variation was

used as a comparison to the base case. A large stack final evaluation was conducted and compared to small stack testing. Testing primarily focused on single cells and small stacks but two full-kilowatt scale tests were conducted to benchmark performance as well. In addition, TMI evaluated fabrication methodologies relating to component quality and the impact on long-term degradation.

Results: Figure 1 shows the operation data of the fuel cell system on natural gas >1,300 hours. In the 1,000-2,000 hour continuous operation range, bulk electrode stability was shown to be a challenge.

Conclusions and Future Directions: Despite these challenges, the demonstration provided valuable operational and engineering information while producing usable electricity for the farm at levels similar to those demonstrated in the laboratory. At approximately 1 kW, the system was able to demonstrate 32.4% electrochemical efficiency on soybean oil at the farm.

The demonstration was successfully completed. The test system was decommissioned on June 16, 2009. A post-operative diagnostic was completed and several additional areas for improvement were identified. Overall, the fuel cells themselves were very effective for the demonstration. The catalyst used for this test was less mechanically stable than would be necessary in a full commercial system and will become an area of development. Work will also continue to improve cell and stack quality and performance to increase efficiency. This work will continue under TMI's business plan toward commercialization.

FY 2009 Publications/Presentations

TMI hosted two meeting sessions at the demonstration site sponsored by the OSC. The sessions were attended by representatives from the OSC, members of the Energy Subcommittee of the Ohio State Legislature, representatives from Senator

FIGURE 1. Stable Operation on Natural Gas for >1,300 Hours

Voinovich's office, representatives of Lockheed-Martin MS2 Division, representatives from the Ohio Agricultural Research and Development Center of The Ohio State University, local business interests, members of the media and the president of the Thomas Edison Birthplace Association, a direct descendent of Thomas Edison.

Catacel Corporation

Project: EFC-H4-9, Novel Stackable Structural Reactor (SSR[®]) for Low-cost Hydrogen Production

Project Objectives

- Prove technology in large-scale hydrogen generation plants.
- Complete product development and support manufacturing scale up and facilitate market insertion.

Accomplishments

- Documented key operating parameters of reference plant
- Manufactured and installed SSR[®] in reference plant – Similar to the recent Borcelik activity, Catacel will manufacture catalyst for the reference plant. This new catalyst will have a modified design based on the output of Task 1 to prevent the red rings. Working with the plant operator, Catacel will remove and store ceramic catalyst from the reference plant, and install SSR[®] using known methods.
- Document improvements in performance.

Introduction/Approach: The Catacel SSR[®] is intended to be a drop-in replacement for conventional ceramic catalyst media in the stationary steam reforming process that has been used for many years to produce hydrogen from natural gas. Current technology requires that the ceramic catalyst bed be replaced every three to five years due to mechanical degradation of the media. The Catacel SSR[®] will eliminate the periodic replacement that is required for ceramic packed beds. SSR[®] is expected to provide a significant capacity increase (~30%) or a significant energy savings (~20%) in most reformers that use this technology. In an existing plant, simple replacement of catalyst with SSR[®] is expected to show a 1-year payback on investment with energy savings.

Results: One potential SSR[®] problem has been observed at Borcelik. Visual inspection of the catalyst tubes through a peep-hole in the furnace while operating shows red bands that seem to be near the end of each individual SSR[®]. Hydro-Chem has expressed some

concern that these bands are hot spots that could lead to eventual tube failure. They have not, as yet, been concerned enough to require action. At this point, nobody knows exactly how hot the bands are, or if in fact they are a problem. Catacel strongly suspects these bands represent areas of reduced heat transfer, which could negatively impact the overall performance of SSR[®] in some way. In any path forward, Catacel must develop an understanding of the cause and affect of these bands and implement any necessary corrective action.

Very positive upside potential to the SSR[®] is being demonstrated by the Borcelik installation. To date the plant has been running for nearly a month. Installation went very smoothly, demonstrating that there is little or no risk to installing SSR[®] in other plants. And there is clear reward to other plants if the expected performance benefits can be realized.

Conclusions and Future Directions: The SSR[®] is proving itself as a viable cost-effective replacement for ceramic catalyst inserts for hydrogen generation. A Borcelik on-site action plan will be devised based on that activity. This plan will likely involve certain measurements to be made during operation, and methods for SSR[®] removal and inspection that will allow verification of the root cause(s). The plan will also provide for quick replacement or repairs to the Borcelik unit based on findings. Appropriate changes will be made to the baseline SSR[®] design which will eliminate the red ring issue.

Faraday Technology, Inc.

Project: EFC-H1-1-2A, Nanocatalyst Development Employing Electrically Mediated Processing for Hydrogen Generation

Project Objectives

Develop a low-cost, mass fabrication technology for catalyzation of membrane electrode assemblies (MEAs) for proton exchange membrane electrolyzers and regenerative fuel cells.

Accomplishments

- A catalyst-coated membrane approach was used to form thin-film MEAs to decrease the Pt-Ir catalyst loading (from 4 to 1.5 mg cm⁻²).
- Demonstrated composition of 85 wt% Pt and 15 wt% Ir shows higher round-trip efficiency (e_{RT}) at investigated current densities.
- Alpha-scale apparatus was tested and configured to produce a uniform distribution of catalyst across a gas diffusion layer.

Introduction/Approach: Utilize sophisticated, high frequency asymmetrical waveforms to electrodeposit optimized loadings of highly dispersed catalyst particles onto support structures, only in regions with access to all the reaction components (high utilization), for incorporation into an MEA.

Results: In electrolyzer mode (Figure 1), the performance of unsupported PtIr catalyzed MEA is higher than that of unsupported Pt catalyzed MEA due to higher reactivity of Pt-Ir catalyst for the oxygen evolution reaction (OER).

Table 1 shows the conversion efficiency values of unitized regenerative fuel cells (URFCs) at different current densities estimated as described in Ioroi et al. The results indicated that the composition of 85 wt% Pt and 15 wt% Ir shows higher round-trip efficiency (ϵ_{RT}) at investigated current densities.

Bifunctional electrocatalysts for oxygen electrode of an URFC were prepared with unsupported Pt and Ir black catalysts. The electrochemically active surface area and oxygen reduction reactivity of 85Pt:15Ir (composition of Pt:Ir is 85:15) was comparable to those of Pt black catalyst (composition of Pt:Ir is 100:0). The

onset potential for OER of the Pt-Ir black catalyst is about 240 mV more negative than that of the Pt black catalyst, which implies that unsupported Pt-Ir black catalyst is more effective than Pt black catalyst for oxygen evolution reaction. Based on the electrochemical characteristics of unsupported Pt-Ir catalyst, it is found that an URFC using 85Pt:15Ir catalyst shows highest round-trip efficiency at different current densities.

Conclusions and Future Directions: The processes and techniques developed in this work lead to implementation of an industrial process to produce in situ alloy deposits for a multitude of applications. For instance, these electrically mediated techniques can be reapplied for the production of solar cells, disinfection electrodes, corrosion production, thin film magnets, etc. Furthermore, the beta-scale reel-to-reel system will reduce the production cost and time, for any of these processes.

Inorganic Specialists, Inc.

Project: EFC-H3-6-1B, Nanofiber Paper for Efficient Hydrogen Generation

Project Objectives

- Demonstrate nanofiber paper for hydrogen production, and compare it to existing products.
- Develop continuous nanofiber papermaking for the hydrogen generation application.
- Compare different methods of catalyst deposition for its impact on hydrogen generation efficiency.

Accomplishments: Nanofiber paper is a platform technology. There are many applications for it beyond fuel cells. During the course of this project, some of these applications were pursued for other programs. The link that relates those other projects to this one is the manufacturing angle. Developing the ability to manufacture is a key milestone that will benefit all of these other embodiments of the paper.

The killer application for nanofiber paper – silicon-coated nanofiber paper as an anode in a lithium ion battery.

- A specially made nanofiber paper was silicon coated by Ultramet. Transmission electron microscopy analysis showed that the coating was about 23 nm thick, and that the sample was about 30% Si by weight. Silicon-coated nanofiber paper shows >1,000 mAh/g of energy storage, with stable cycling and low first-cycle irreversible loss. This is breakthrough, transformational technology of huge importance. A patent application has been filed.

FIGURE 1. Current-Voltage Curves of Different Pt-Ir Catalysts in Water Electrolyzer Mode at 20°C

TABLE 1. Energy Conversion Efficiency of an URFC with various compositions of Pt-Ir Catalysts

Current density (mA cm ⁻²)	Composition of Pt and Ir	V _{FC} (V)	V _{WE} (V)	ϵ_{RT} (%)
50	100 : 0	0.832	1.71	49
	85 : 15	0.802	1.562	51
	70 : 30	0.652	1.516	43
	40 : 60	0.518	1.520	34
100	100 : 0	0.775	1.776	44
	85 : 15	0.740	1.645	45
	70 : 30	0.545	1.622	34
	40 : 60	0.313	1.592	20

High Density Nanofiber Paper for Thermal

Conduction: As part of a state-funded project, Graftech is interested in the papermaking approach as a way to make a high thermal conductivity material from nanofibers. Some samples have been provided to them for their analysis. Some of these had densities as high as 0.84 g/cc (normally the paper is closer to 0.2 g/cc). Other similar samples have been sold to Eaton Industries for the same purpose.

- **Other Electrolysis Testing:** Nanofiber paper samples for hydrogen electrolysis from ammonia were prepared and sent to Prof. Botte at Ohio University in Athens. Prof. Botte will electroplate her catalyst onto these materials, and test them in her EMTEC-funded work. We are furnishing her three types of nanofiber paper.
- **Gas Diffusion Layer Material:** During this project we were approached by a major auto manufacturer, and subsequently sold them sheets of hydrophobic-treated nanofiber paper made to their specs for evaluation as gas diffusers in fuel cells. This is another potential fuel-cell-related product for nanofiber paper.
- **Larger Size Handsheets:** An apparatus was constructed to prepare extra large sheets (18"x18") of nanofiber paper for an Air Force Proproject.
- **Aerospace Composites:** During the project, individual sheets of nanofiber paper that were 12"x 12" in dimension and 10-20 mils thick were prepared for both Lockheed Martin and Boeing.
- **Nanofiber Paper with Nickel Nanostrands:** A paper variety with a heavy content of nickel nanostrands was prepared for an Air Force Proproject, and tested for its Lightning Strike protection.
- **Modifications of Commercial Fuel Cell Products:** A project is currently underway with BASF to modify their commercial fuel cell anodes and cathodes with nanofibers to improve their catalyst utilization and performance.

Introduction/Approach: Our studies have shown that nanofiber paper produces excellent catalyst utilization in fuel cells. Thus it makes sense to examine electrolyzers, which are essentially fuel cells operated in reverse, to see if the high surface area and catalytic enhancement of the nanofiber paper produces high efficiency, high output hydrogen generation (Figure 1). Furthermore, the practical application of this technology hinges on being able to make nanofiber paper commercially, and so the project includes the development of the first demonstration unit for continuous nanofiber papermaking.

Results: Test samples were prepared by modifying commercial MEA backings with combinations of hydrophobic and hydrophilic carbon nanofibers. Five

FIGURE 1. Water Electrolyzer System to be used to Evaluate Nanofiber Papers as Catalyst Substrates

different combinations were examined. The first was made with pure hydrophobic nanofibers (labeled '0'). Then there were MEA samples made from hydrophilic/hydrophobic mixes of 25%, 50% and 75% (labeled '25', '50' and '75', respectively). The purely hydrophilic nanofiber MEA was referred to as '100'.

The performance of the nanfiber MEAs shown in Table 1 did not match that of the standard. The first test at the low current of 35 mA resulted in similar efficiencies ~50% from all of the samples. However at higher currents the majority of the MEAs exhibited poorer efficiencies. The exception was the 25% hydrophilic sample, which maintained reasonable efficiency at all current levels, but still did not outperform the Toray standard. Note for the '0' and '50' samples at 75 mA the efficiency was so poor that the potential was beyond the measurable limit of the galvanostat. In these instances no reliable efficiency can be calculated, which is why these results are missing from Table 1. We can estimate that on those two occasions the efficiency would have been less than 10%

Further evidence of the degradation of the samples was observable with the potential sweep experiments. Examples of the potential sweeps of two samples '100' and '25' are presented in Figure 2. Initial scans were similar to the Toray standard peaking at ~-2 V and

TABLE 1. Performance of Nanofiber MEAs

	35 mA	55 mA	75 mA
Toray	57%	54%	59%
0	25%	11%	x
25	58%	50%	41%
50	49%	9%	x
75	48%	40%	32%
100	43%	36%	18%

FIGURE 2. Potential Response of '100' and '25' when the Current was Swept to -80 mA

-80 mA. However subsequent runs failed to reproduce the initial performance. For the 100% hydrophilic sample each sweep was substantially worse than the previous one, until the last two sweeps hit the galvanostat's measuring limits. The best nanofiber sample ('25') also failed to reproduce its first sweep but did at least become consistent with sweeps that would

plateau to ~4 V at -80 mA. Even though this stability was the best seen of all of the nanofiber samples it was still worse than the Toray standard.

Conclusions and Future Directions: Our conclusion is that nanofiber samples prepared in this way (thin coatings on commercial supports, with sprayed-on catalyst) do not perform better than standard commercial electrolysis materials. The best sample which was made up of 25% hydrophilic and 75% hydrophobic nanofibers was not significantly different from the Toray standard at low current densities.

This behavior is in contrast to enormous performance improvements seen in a fuel cell configuration for both methanol oxidation and oxygen reduction. This implies that the advantages gained from nanofibers in the hydrogen and methanol oxidation reactions are of no consequence in the hydrolysis reaction. This was by no means an exhaustive study and it may still be possible for a nanofiber MEA to outperform a Toray MEA. Other parameters that may affect an MEA's performance should be considered (e.g. fabrication variables like pressing at higher temperatures). To create an electrolysis MEA with radically better properties will probably require a different fabrication process. Catalyzed nanofiber paper has been shown to enhance the performance of fuel cells through improved catalyst utilization. This project sought to translate those benefits to the reverse process of a fuel cell, electrolysis and hydrogen generation. It was ultimately found that the turbulent conditions and/or stressful voltages that accompany electrolysis were not compatible with the morphology of our catalysts on our nanofibers. Although we cannot rule out that the approach itself has merit, the procedures and materials we examined did not give the results that were sought.

Nonetheless, the design and creation of the first carbon nanofiber papermaking unit was a major achievement from this project. Nanofiber paper is a platform technology for a host of energy-related and composite applications, and the ability to manufacture it represents a true milestone in transitioning it from the lab to the commercial sphere.

II.J.3 Hydrogen Production and Fuel Cell Research*

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Subcontractor:
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*Congressionally directed project

Technical Targets

This project is conducting experimental studies of UT-3 thermochemical cycle and its improvement in the cyclic performance for hydrogen production. On the basis of these studies, thermodynamic analysis of the cycle will be conducted to evaluate economical feasibility.

- Process energy efficiency: 40%

Approach

- Evaluation of characteristics of calcium and iron oxide solid reactant to improve their formulation.
- Chemical kinetic studies to evaluate and improve the solid reactant's cyclic life, reaction rates and conversion using lab-scale apparatus.
- Experiments on the feasibility of UT-3 thermochemical cycle for hydrogen production.
- Fabrication and evaluation of porous CaO and Fe_3O_4 reactants which have an enduring structure and favorable characteristics in cyclic transformations between oxide and bromide forms.

Accomplishments

- An attempt was made to increase the calcium oxide content through repetitive impregnation steps and resulted in higher calcium oxide contents in the samples.
- Cyclic performance of the samples with various calcium oxide contents was examined for the first cycle.
- Thermal efficiency of the UT-3 process was evaluated considering inert materials, heat recovery and incomplete conversion.
- In order to determine feasible heat recovery in the process, pinch analysis was employed in this thermodynamic analysis.

Conclusions

Calcium oxide fabric samples with higher calcium oxide contents were fabricated and evaluated for the first cycle. The hydrolysis rate was retarded with increasing the calcium oxide contents. Practical process efficiency was determined using the experimental results and theoretical thermodynamic analysis. It was found that the effect of heat recovery and inert materials cannot be disregarded in the calculation of thermal efficiency of the cycle. To increase the efficiency, heat recovery must be used and the use of the inert materials should be minimized.

Task 1. Thermochemical Hydrogen Production

Objectives

- Investigate UT-3 thermochemical cycle and conduct kinetic studies.
- Improve stability and performance of solid reactants for cyclic gas-solid reactions.
- Lower hydrogen production cost by increasing hydrogen yield with an improved pellet formulation.
- Reduce operating cost by lowering the reactor operating temperatures.

Technical Barriers

This project addresses the following technical barriers from the High-Temperature Thermochemical, Solar-Driven Production of Hydrogen section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

(U) High Temperature Thermochemical Technology

Task 2. Hydrogen Production from Biomass

Objectives

Improve the hydrogen production process of conventional biomass gasification and reduce capital cost by combining steps. In the present approach, the aim is to combine the two step shift and pressure swing adsorption separation into a single step by integrating biomass steam gasification, CO₂ removal and hydrogen separation. The project also aims to improve the total hydrogen yield and overall process efficiency.

Technical Barriers

This project addresses the following technical barriers from the Biomass Gasification/Pyrolysis Hydrogen Production section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

(T) Capital Cost and Efficiency of Biomass Gasification/Pyrolysis Technology

Technical Targets

Our research aims to enhance the hydrogen yield of conventional biomass steam gasification by using simple inexpensive sorbents such as calcium oxide. The sorbent absorbs one of the co-products of gasification (namely CO₂) and thereby shifts the equilibrium in favor of additional hydrogen. Theoretical simulations and experimental studies have shown a substantial improvement in hydrogen yield. The insights gained from these studies will be applied towards further experimental investigation and regeneration of spent sorbent. The following DOE 2010 energy efficiency and hydrogen production cost are targeted:

- Energy Efficiency¹: 50%;
- Plant gate cost²: \$1.75/gge H₂

¹Efficiency defined as energy of hydrogen out of the process (lower heating value of hydrogen) divided sum of energies into the process (lower heating value of feedstock and all other energies needed).

²gge: gasoline gallon equivalent.

Approach

Biomass feedstock common to Florida such as pine mulch was steam gasified in a batch type reactor. The effects of temperature and presence of sorbent (calcium oxide) and form of sorbent (powder vs pellets) on the hydrogen yield were experimentally investigated. The initial experimental studies have shown a significant improvement in hydrogen and overall gas yield in presence of sorbents. In order to enhance cyclic

performance of the sorbents, a simple and effective immobilization technique of the calcium oxide sorbent in fibrous ceramic mat as a substrate was developed and the cyclic performance was evaluated.

Accomplishments

- Two calcium oxide absorbent samples using different materials of fabric, alumina and yttria, were fabricated for the severe calcination condition.
- The cyclic carbonation-calcination experiments of the two samples were conducted under the severe calcination condition, with 20% CO₂ at 850°C.
- Dolomite on alumina fabric was used in the preparation of the absorbent sample.
- Two samples were prepared of dolomite applied to alumina fabric and yttria fabric.
- The two samples were then analyzed using the thermogravimetric analysis.

Results

The use of dolomite is being investigated in this study as previous researchers have discovered that the inert magnesium oxide in dolomite contributes to stabilizing the structure of the solid sorbent in the multi-cycle carbonation-calcination process. One issue that arises as a result of using calcium oxide to capture carbon dioxide is that, at first the carbonation cycle is very fast as the carbon dioxide molecules are captured by the surface calcium oxide converting the calcium oxide into calcium carbonate. As the reaction proceeds it becomes difficult and takes longer for the carbon dioxide to get to the available interior calcium oxide in the structure. Since, magnesium carbonate has a lower decomposition temperature than calcium carbonate it improves access for the carbon dioxide molecules to react with the interior calcium oxide molecules available.

Initial data collected showed that dolomite was comparable to the calcium oxide in the capture of carbon dioxide. However, to make an accurate comparison to determine the efficiency and conversion ability of each compound further experimentation is required at the same conditions for each compound. Figure 1 shows the dolomite sample on the alumina fabric during a four hour carbonation/calcination cyclic run.

Conclusions

- Dolomite is being investigated to determine if the University of South Florida sorbent preparation method will increase the carbon dioxide capture capability and capacity.
- Carbon dioxide can be captured by dolomite type material using the inexpensive preparation method developed by the University of South Florida.

FIGURE 1. Cyclic Carbonation and Calcinations of Dolomite on Alumina Fabric

Task 3. Photoelectrochemical Hydrogen Production

Objectives

Overall

- To produce H_2 in the \$0.70–2.00/kg range
- Photocatalyst efficiency (sunlight to H_2) = 14%
- Photocatalyst cost (\$70/m²)
- Membrane cost (\$50/m²)
- Develop catalytic thin films that can function with a photoelectrochemical device

Current

- To develop tandem solar cells to meet the above efficiency and cost objectives.
- Current emphasis is on development of the p-window contact for CdSe in the CdSe/Si(CIGS) tandem structure.

Technical Barriers

This project addresses the following technical barriers from the Photoelectrochemical Hydrogen Production section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (Y) Materials Efficiency
- (Z) Materials Durability

Approach

- Device Structures
 - CdSe/Si – intermediate term, hybrid.
 - CdSe/CIGS – long-term, thin-film, low-cost.
- Key Technology Limitation
 - High efficiency, transparent p-window/CdSe/n-window device.

- The p-window is limiting performance because of low voltage open circuit.
- Current Focus
 - Development of ZnSe and ZnTeSe as p-windows.
 - Improving doping efficiency to increase voltage open circuit by use of ion source implantation of nitrogen.

Accomplishments

- Ion source implantation of N interferes with stoichiometry control in $ZnSe_xTe_{1-x}$:N p-window contacts except at low Te levels.
- Use of ZnTe/ZnSe:N superlattice structures allows better control at higher Te levels.

Summary and Future Work

- Significant improvement in window p-layer doping has been accomplished.
- Concomitant improvement in voltage open circuit has been realized.
- Additional techniques will be pursued to further improve doping and voltage open circuit:
 - Direct doping of $ZnSe_xTe_{1-x}$ p-window contacts with Cu.
 - Co-doping of $ZnSe_xTe_{1-x}$ p-window contacts.

Task 4. Photocatalytic Hydrogen Production

Objectives

Optimize mechanochemical treatment parameters (duration of ball-milling treatment, temperature and duration of post annealing).

Technical Barriers

This project addresses the following technical barriers from the Photoelectrochemical Hydrogen Production section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (AP) Materials Efficiency
- (AQ) Materials Quality
- (AR) Efficiency

Technical Targets

Design and synthesis of photocatalytic materials that meet the following DOE 2010 Photoelectrochemical Hydrogen Production targets:

- Chemical conversion process efficiency >10%
- Durability, >1,000 hrs

Approach

(i) Photocatalytic efficiency of modified TiO_2 based on the photodegradation kinetics of methyl orange.
 (ii) Correlation of photocatalytic properties with optical, bonding, structural and microstructural characteristics. Attempts were made to improve the photocatalytic behavior of TiO_2 by doping with various concentrations of Zn (0, 1.3, 2.2, 3.1, 4.0 and 4.9) in the sol-gel process.

Accomplishments

- Modified by ball-milling TiO_2 catalyst having improved efficiency.
- Optimized duration and temperature of thermochemical method for N-doping of TiO_2 .

Results

Figure 2 shows the dependence of initial rate of methyl orange degradation on the TiO_2 catalyst thermochemical treatment duration at two different temperature treatments, namely, 625°C and 550°C.

The most effective decomposition of methyl orange was observed with the thermochemical treatment temperature of 625°C and the treatment duration from 2 to 3 hours. The optimized thermochemically treated photocatalyst is at least four times more efficient than the untreated samples.

Conclusions

- Attempts were made to improve the photocatalytic behavior of TiO_2 by doping with various

FIGURE 2. Dependence of initial rate of methyl orange degradation on the TiO_2 catalysts treated thermo-chemically at 625°C and 550°C.

concentrations of Zn (0, 1.3, 2.2, 3.1, 4.0 and 4.9) in the sol-gel process.

- There is no significant change in the photocatalytic efficiency for TiO_2 -Xwt% Zn at two different calcination temperatures (500 and 600°C).
- The reason for this may be due to the large crystallite sizes and the lower surface area of these initial samples.

Task 5. Development of High Performance, Low Cost PEM Electrolytes

Objectives

- Decrease cost per unit power for proton electrolyte membranes (PEMs).
- Improve long-term chemical stability of fuel cell PEM electrolytes operating at $\leq 120^\circ\text{C}$.
- Maintain or improve high protonic conductivity of PEM electrolytes.
- Minimize water content necessary to support high conductivity under stated conditions.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) Durability
- (B) Cost
- (C) Performance

Technical Targets

This project is performing chemical modifications of polyether ether ether ketone polymer (PEEK), converting it into a PEM electrolyte. Insights gained from these studies will be applied toward the design and synthesis of PEMs that meet the following DOE 2010 technical targets targets:

- Operating temperature: 120°C
- Conductivity at operating temperature: 0.1 S/cm
- Room temperature conductivity: 0.07 S/cm
- Inlet water vapor partial pressure: 25 kPa
- Cost: \$20/m²
- Durability: 2,000 h at $>80^\circ\text{C}$

Accomplishments

- Successfully prepared via cross-linking chemistry a membrane based on highly sulfonated (water soluble)

sulfonated poly(ether ether ketone) (SPEEK), with an equivalent weight of 534 g/equivalent weight (EW).

- Developed a synthetic approach for fabricating a proton exchange membrane made from the fluorosulfonic acid of PEEK. The procedure begins with bromination of the bis-acetamide derivative of 2,5-diaminobenzotrifluoride. Have successfully performed the amidization, the monobromination, and the sulfatodehalogenation of the starting material.
- Developed multiple characterization methods for monitoring peroxide attack.

Conclusion

Water uptake is an important attribute of all membrane electrolytes, as it is related to mechanical strength, creep, and dimensional stability. Thus some means of controlling water uptake by a hydrophilic sulfonic acid polymer is desirable. This is particularly important for SPEEK, which at high degrees of sulfonation (i.e., low EW) has demonstrated substantial water uptake, on order of 10's of water molecules per sulfonic acid unit. We have attempted to control water uptake in SPEEK membranes by performing cross-linking reactions on the finished polymer. Water-soluble SPEEK (85% degree of sulfonation, or 418 g/EW), benzene dimethanol, and various transition metal chloride catalysts were cast together to form a membrane that was heated at 200°C for 10 min. The resulting insoluble membrane was shown to have conductivity comparable to an uncross-linked SPEEK membrane over a range of relative humidities.

Task 6. PEM Fuel Cell Freeze Degradation

Objectives

- Quantify a PEM fuel cell's power degradation resulting from subzero climate exposure.
- Develop a performance map for the membrane following the subzero temperature storage of the cell.
- Determine the effectiveness of industry accepted mitigation schemes at the Departments of Energy's operational limits.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) Durability
- (B) Cost

Technical Targets

The goal of this research is to determine the amount of performance degradation experienced by a PEM fuel cell after being exposed to several freeze/thaw cycles at various subzero temperatures and humidification levels.

- Determination of critical membrane conditions in order minimize the subzero storage degradation.

Approach

Several membrane electrode assemblies with similar pore size, platinum content, and fabrication technique were subjected to freeze/thaw cycles at varying temperatures and levels of humidity. After each cycle was conducted a complete power profile was developed for each membrane. The profile was compared to the base line power profiles obtained before the first freeze/thaw cycle to obtain the inherent power loss.

Accomplishments

- Determined that current commercial fuel cell technology has progressed to meet the Department of Energy's goal of survivability to -40 degrees Celsius.
- Identified that the duration of subzero storage has a very strong influence on the amount of degradation experienced by the cell.

Conclusions

It can be seen from the results that the duration of the freeze/thaw cycle has the greatest effect on the internal ice formation and therefore the performance degradation exhibited by the membrane. The other operational parameters still may have a significant effect, but it is clear the internal ice takes a significant amount of time to form with in the cell. This ability to delay or inhibit the ice formation is probably a result of the polytetrafluoroethylene coating applied to the gas diffusion layer of the membrane electrode assembly.

Patents Issued

1. Yogi Goswami, Man Su Lee, Nikhil Kothurkar and Elias K. Stefanakos, "Carbon Dioxide Sequestration", submitted as a US provisional patent, #61/013,844, USF Ref. No. 07B109PR, Dec.14, 2007.
2. Kislov, N., Schmidt, M., Kothurkar, N., Stefanakos, E., and Goswami, Y. "Method and Process for Producing Titanium Dioxide Exhibiting an Improved Photocatalytic Activity. Submitted on January 26, 2007 USF Ref. No.: 07A014PR (Provisional Patent).

FY 2009 Publications/Presentations

1. Man Su Lee, Yogi Goswami and Elias K. Stefanakos, "Immobilization of calcium oxide solid reactant on a yttria fabric and thermodynamic analysis of UT-3 thermochemical hydrogen production cycle", Accepted for the publication in International Journal of Hydrogen Energy.
2. Madhukar R. Mahishi, M. S. Sadrameli, Sanjay Vijayaraghavan and Yogi Goswami, "A Novel Approach to Enhance the Hydrogen Yield of Biomass Gasification Using CO₂ Sorbent", J. Eng. Gas Turbines Power January 2008 Volume 130, Issue 1.
3. Man Su Lee, Yogi Goswami, Nikhil Kothurkar and Elias K. Stefanakos, "Immobilization of calcium oxide absorbent on a fibrous alumina mat for high temperature carbon dioxide capture", ASME Energy Sustainability 2008.
4. J. Gass, H. Srikanth, H.; N. Kislov, S.S. Srinivasan, Y. Emirov, Magnetization and magnetocaloric effect in ball-milled zinc ferrite powder, *Journal of Applied Physics* (2008), 103(7, Pt. 2), 07B309/1-07B309/3.
5. N. Kislov, S.S. Srinivasan, Yu. Emirov, E.K. Stefanakos, Optical absorption red and blue shifts in ZnFe₂O₄ nanoparticles, *Materials Science and Engineering B*, 2008, DOI: 10.1016/j.mseb.2008.10.032, In Press.

III. HYDROGEN DELIVERY

III.0 Hydrogen Delivery Sub-Program Overview

Introduction

Hydrogen must be transported from the production site to a fueling station or stationary power site or produced on-site. It also must be compressed, stored and dispensed at refueling stations or for stationary power generation. Due to its relatively low volumetric energy density, current transportation, storage, and final delivery entail significant costs and inefficiencies for hydrogen as an energy carrier. The Hydrogen Delivery Sub-Program activity focuses on developing technologies to reduce the cost and increase the energy efficiency of hydrogen delivery during the mid-term and long-term use of hydrogen as a major energy carrier.

Three potential delivery pathways are being considered: gaseous hydrogen (trucks or pipelines), liquid hydrogen (trucks), and novel solid or liquid hydrogen carriers (trucks or pipeline). A carrier is a material that stores hydrogen at lower pressures and higher temperatures. Examples of potential hydrogen carriers include metal or chemical hydrides, nanostructures, and liquid hydrocarbons that can be easily dehydrogenated and re-hydrogenated with a round-trip efficiency greater than 60%.

Goal

Develop hydrogen delivery technologies that enable the introduction and long-term viability of hydrogen as an energy carrier for transportation and stationary power.

Objectives

- By 2012, reduce the cost of compression, storage and dispensing at refueling stations and stationary power facilities to <\$0.80/gasoline gallon equivalent (gge) of hydrogen (independent of transport). By 2017, reduce this cost to <\$0.40/gge.
- By 2014, reduce the cost of hydrogen transport from central and semi-central production facilities to the gate of refueling stations and other end-users to <\$0.90/gge of hydrogen. By 2019, reduce this cost to <\$0.60/gge.
- By 2019, reduce the cost of hydrogen delivery from the point of production to the point of use in vehicles or stationary power units to <\$1.00/gge of hydrogen in total.

Fiscal Year 2009 Technology Status

Current costs for the transport of hydrogen range from \$3 to \$9/gge. This is based on transport by gaseous tube trailers or cryogenic liquid tank trucks and is dependent on the quantity of hydrogen and distance that the hydrogen is transported. Pipeline transport costs are at the lower end of the costs range, and are also dependent on transport distance and quantities. These transport costs do not include the delivery costs associated with compression, storage and dispensing at fueling sites. These additional costs could be as high as \$2-3/gge of hydrogen.

In order to achieve the long-term goal of \$1/gge for the cost of hydrogen delivery, and to have commercially viable costs during the transition period, significant technology development is needed. Challenges to be overcome include:

- **Pipelines:** resolve hydrogen embrittlement concerns with steel pipelines, reduce capital costs by developing new steel compositions and/or welding and installation techniques, and/or develop viable composite pipeline technology with reduced capital costs.
- **Tube Trailers:** increase gaseous tube trailer capacity and lower trailer costs to reduce overall hydrogen delivery cost, especially during a market transition.
- **Compression:** develop more reliable and lower cost hydrogen compression technology for pipeline transmission and stationary as well as refueling station applications.

- **Storage:** develop lower capital cost off-board storage technology; confirm the technical feasibility and adequate availability geologic storage for hydrogen.
- **Liquefaction:** reduce the capital cost and increase the energy efficiency of hydrogen liquefiers.
- **Carriers:** leverage the National Hydrogen Storage Project for on-board storage applications to determine if a novel solid or liquid carrier might be suitable for hydrogen transport or off-board storage and result in lower delivery costs and higher energy efficiency.
- **Analysis:** comprehensive analysis of the options and trade-offs of hydrogen delivery approaches for the near-term and long-term.

FY 2009 Accomplishments

- To overcome the embrittlement and capital cost concerns of steel pipeline materials, research is being conducted on fiber reinforced polymer (FRP) pipelines. In FY 2009, researchers at Oak Ridge National Laboratory and Savannah River National Laboratory (SRNL) concluded a testing regimen on a commercially available FRP pipeline material and achieved the following:
 - Hydrogen compatibility tests following eight months of accelerated-aging tests (equivalent to five or more years at room temperature) showed no degradation.
 - Pipeline material passed blow-down testing.
 - The leakage rate for the FRP pipeline was measured to be less than 0.02 percent, compared with the 2017 target leakage rate of less than 0.5 percent.
 - The measured leakage rate of a pipeline joint was approximately 0.5 kg H₂ per year per joint.
- SRNL and the American Society of Mechanical Engineers (ASME) also prepared an action plan that outlines the necessary elements for design and life management of FRP for hydrogen service. Life management is a process for assessing and mitigating pipeline risks in an effort to reduce both the likelihood and consequences of incidents. This paper is the first step towards the development of the necessary ASME codes for FRP hydrogen pipeline delivery.
- Work continued to increase the capacity (currently approximately 300 kg H₂) while reducing the cost of gaseous tube trailers.
 - Lincoln Composites developed the design and manufacturing procedures for the 600 kg H₂ tanks, including large-scale dome molding and tubular welding; filament winding; curing and coating; and proof testing. The tanks passed both burst and penetration (gun fire) testing.
 - Lawrence Livermore National Laboratory continued their work to develop an innovative tube trailer design that would triple the capacity to 1,100 kg H₂ through the use of high-strength, low-cost glass fiber instead of carbon fiber. The researchers demonstrated that the glass fiber strength is 80 percent higher at 140 K versus 300 K. To optimize the strength of the glass fiber, the tube trailer would transport cold or cryo-compressed hydrogen. Glass fiber also has the added benefit of a substantially reduced cost (\$6/kg for glass fiber vs. \$23/kg for carbon fiber) resulting in a 50 percent trailer cost reduction (\$200,000 instead of \$400,000) while holding three times as much hydrogen.
- Compression will be needed at various points throughout the hydrogen delivery infrastructure and researchers are making progress on lower cost, higher reliability hydrogen compressors.
 - The use of mass produced components could result in a dramatic cost savings for compressors, especially in early markets. Concepts NREC is developing a centrifugal compressor for hydrogen made from off-the-shelf components designed for natural gas service. Concepts NREC evaluated 30 compressor-gearbox configurations, materials, and compressor-drive options, and determined the best combination of components.
 - FuelCell Energy increased the capability of their compressors from 3,000 psi to 4,500 psi in a single-stage electrochemical compression cell. By decreasing the number of stages required to compress hydrogen, they can lower the capital costs. FuelCell Energy completed over 1,000 pressure cycles without a performance loss. That work may ultimately reduce compressor

maintenance costs and compressor downtime. These two aspects are major contributors to delivery cost and bring the program closer towards the 2017 goal of highly-reliable compressors at both the forecourt and potentially for pipelines.

- Progress was made in lowering the cost of liquefaction.
 - Prometheus is working on an innovative liquefier called the Active Magnetic Regenerative Liquefier. Utilizing magnetic cooling, this could reduce the energy by 50% as compared to conventional gas expander liquefiers, and may reduce the capital costs to liquefy hydrogen by 30%, therefore bringing the program closer to reaching the goal of \$1/kg of delivered hydrogen. In 2009, they completed the design for and began construction of their lab-scale magnetic hydrogen liquefier prototype. The prototype will be the first demonstration of the concept.
- A number of accomplishments were also made in hydrogen delivery analysis.
 - Argonne National Laboratory (ANL) added 700 bar fueling and cryo-compressed fueling to the Hydrogen Delivery Scenario Analysis Model (HDSAM). They found, among other things, that 700 bar gaseous hydrogen (GH₂) fueling employing a high pressure cascade system was only 15% more expensive than 350 bar GH₂ fueling. In addition, ANL showed that hydrogen station costs for 700 bar vehicles using booster compressors was 70% higher than the station cost for filling cryo-compressed vehicles with a cryopump.
 - The National Renewable Energy Laboratory designed a preliminary version of the Hydrogen Rail Components Model to be used as an add-on to the HDSAM model. The model allowed them to calculate the costs of delivering hydrogen via the rail network. Rail delivery appears to be a viable low-cost option for long distance transport.

Budget

The President's FY 2010 Hydrogen Delivery budget request was \$0 as the program refocuses efforts toward near-term fuel cell technologies that include stationary, portable, and specialty applications, e.g., fork lifts.

2010 Plans

Final reports documenting progress will be issued in FY 2010. The applied research and development program in the Office of Energy Efficiency and Renewable Energy will coordinate with the Office of Science, which plans to include up to \$50M of basic research related to hydrogen and fuel cell technologies. Through basic science activities, a fundamental understanding of issues such as hydrogen embrittlement can help address the challenges of hydrogen technologies in the long term. In addition, through the development projects funded by the American Recovery and Reinvestment Act of 2009, lessons learned and best practices related to hydrogen delivery technologies will be determined.

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III.1 Hydrogen Delivery Infrastructure Analysis

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Partners:

- National Renewable Energy Laboratory (NREL), Golden, CO
- Pacific Northwest National Laboratory (PNNL), Richland, WA

Objectives

- Refine technical and cost data in the Hydrogen Delivery Scenario Analysis Model (HDSAM) to incorporate additional industry input and evolving technology improvements.
- Expand the model to include advanced technologies and other pathway options leading to new versions of the models.
- Improve methodologies for estimating key aspects of delivery system operation and optimizing cost and performance parameters.
- Explore options to reduce hydrogen delivery cost, including higher pressure and/or lower temperature gases, and operating strategies.
- Provide analyses to support recommended hydrogen delivery strategies for initial and long-term use of hydrogen as a major energy carrier.

Technical Barriers

This project directly addresses Technical Barrier A (which implicitly includes Barriers B through F, H and J) of the Delivery Technical Plan in the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan. These are:

- (A) Lack of Hydrogen/Carrier and Infrastructure Options Analysis
- (B) Reliability and Cost of Hydrogen Compression
- (C) Cost and Efficiency of Hydrogen Liquefaction
- (D) Cost of Pipelines
- (E) Cost of Solid and Liquid Carrier Systems

(F) Cost of Gaseous Storage and Tube Trailer Delivery

(H) Geologic Storage

(J) Refueling Site/Terminal Operations

Technical Targets

The project is developing a computer model to evaluate alternative delivery infrastructure systems. Insights from the model are being used to help identify an optimized delivery system which meets the long-term DOE delivery cost target of <\$1.00/gge, including the cost of hydrogen conditioning, purification, transport and operations at the fueling site.

Accomplishments

- Added three new delivery pathways – involving high-pressure gaseous tube trailers, 700 bar gaseous hydrogen dispensing and cryo-compressed dispensing – to the HDSAM.
- Characterized two different station configurations (a high-pressure cascade system or a lower pressure cascade system with dedicated boost compressors for each hose) for 700 bar dispensing and developed a graphical user interface (GUI) to permit users to select a preferred configuration.
- Examined the relationship between peak demand for hydrogen and delivery cost. Explored scenarios involving “flatter” demand profiles.
- Further improved techniques for sizing pathway components and for optimizing compression and storage at the fuel station.
- Examined data on the purity of delivered hydrogen and the limits of existing test methods. Reviewed progress on developing improved test methods and developed an initial estimate of the cost impact of on-site pressure swing adsorption polishing.
- Revised station footprints to better reflect minimum separation distances between different components.
- Completed an updated and expanded version (V 2.1) of HDSAM and an associated Users’ Guide for posting on the DOE Web site.

Introduction

As part of the H2A project, which was initiated in 2003, Version 1.0 of HDSAM was released on the H2A Web site in April 2006 following extensive beta testing and peer review. HDSAM is an Excel-based tool that uses a design calculation approach to

estimate the contribution of individual components of delivery infrastructure to hydrogen cost. Each of those components is described in an individual spreadsheet or tab. The model links the individual components in a systematic market setting to develop capacity/flow parameters for a complete hydrogen delivery infrastructure. Using that systems level perspective, HDSAM calculates full, levelized cost (i.e., summed across all components) of hydrogen delivery, accounting for losses and tradeoffs among the various component costs. A GUI permits users to specify a scenario of interest. A detailed User's Guide and access to the DOE help desk also assist users in running HDSAM.

HDSAM Version 2.0 was released in May 2008. Since then, work has continued on expanding pathways; updating the data base to reflect new analyses, technologies and operating data; and using the model to examine alternative delivery strategies.

Results

In Fiscal Year 2009 HDSAM was augmented with several additional pathways and user options. Three completely new pathways were added to the model: (a) high-pressure gaseous delivery (GH2), (b) 700 bar compressed hydrogen (CH2) dispensing with liquid or gaseous delivery, and (c) cryo-compressed hydrogen (cCH2) dispensing with liquid hydrogen (LH2) delivery.

- For high-pressure gaseous delivery, a \$350,000 7,000 psi (480 bar) compressed gas tube trailer with 700 kg usable capacity is characterized.
- For 700-bar refueling, two station configurations are defined – a high pressure cascade system or a lower pressure cascade system with dedicated boost compressors. Figure 1 shows these options. For the high pressure cascade option, key assumptions include refrigeration to -40°C between the boost

Booster Compression

High Pressure Cascade

FIGURE 1. HDSAM Characterizes Two 700 Bar Hydrogen Fuel Station Configurations

compressor and the dispenser, a refrigeration requirement of 15 ton for a 1,000 kg/d station at a cost of \$6,000/ton, and cascade storage at \$1,450/kg (uninstalled). For the booster compression configuration, key assumptions include the same refrigeration requirements and one booster compressor per hose at an uninstalled unit cost of \$167,000. For either configuration, gaseous hydrogen can be delivered from a centralized production location or terminal via pipeline or tube trailer.

- For the cCH2 pathway, LH2 is delivered via cryogenic tanker truck, stored as a liquid, and dispensed at 250-350 bar. Cryo-pumps, with a capacity of 100 kg/hr at 350 bar, are assumed to cost \$260,000 uninstalled.

The enhanced model was used to investigate alternative technologies, equipment configurations and operating regimes. The delivery infrastructure team (Argonne, NREL and PNNL) contributed advice and assistance on model logic, data and quality assurance. Model updates also underwent an extensive peer-review process within the broader hydrogen modeling community.

As shown in Figure 2, the cost of hydrogen delivery (in \$/kg) varies both with pathway and with station configuration. LH2 delivery drops with cCH2 dispensing since it uses a cryo-pump in lieu of an evaporator and cascade charging system. Higher pressure fueling increases both total delivery cost and the refueling station portion of that cost, especially for the booster compression configuration. The cost of pipeline delivery with 700 bar dispensing is comparable to that of LH2 delivery with cryo-compressed dispensing.

Station costs can be substantially less with cCh2 dispensing. As highlighted in Figure 3, initial capital is nearly 70 percent lower for a LH2 station with cryo-compressed dispensing than for a GH2 station using high-pressure tube storage and 700 bar dispensing.

FIGURE 2. LH2 Delivery Cost Decreases with cCH2 Dispensing, Becoming Comparable to Pipeline Delivery with 700 Bar Dispensing

HDSAM also computes energy use and greenhouse gas (GHG) emissions associated with all pathways, on either a well-to-pump (WTP, i.e., including all fuels and feedstocks from hydrogen production to its dispensing onto a vehicle) or well-to-wheels (WTW, i.e., WTP, as well as to and including vehicle operation) basis. In FY 2009, energy and GHG estimation capabilities were completed for all model enhancements undertaken this year. Figure 4 displays WTW GHG emissions for several of these pathways. Note that although liquefaction is extremely energy intensive, the combination of downstream delivery and dispensing efficiencies as well as equivalent fuel production and vehicle use narrow the difference in WTW GHG emissions between LH2 and other pathways.

In FY 2009, the enhanced HDSAM was also used to investigate the impact of a number of operational and technical changes on the cost of hydrogen

FIGURE 3. Initial Capital Can Be Reduced by Nearly 70 Percent with LH2 Delivery and cCH2 Dispensing As Compared with High Pressure GH2 Delivery and 700 Bar Dispensing

FIGURE 4. Including Hydrogen Production and Vehicle Operation, Differences in WTW Greenhouse Gas Emissions among Delivery Options Narrow

delivery. These included strategies to encourage a “flatter” demand for hydrogen at refueling stations, improvements in compressor reliability, and the addition of on-site polishing to bring delivered GH2 up to fuel cell specifications.

Conclusions and Future Directions

Hydrogen delivery infrastructure analysis seeks to identify aspects of hydrogen delivery that are likely to be especially costly (in capital and operating cost, energy and GHG emissions) and estimate the impact of alternative conditioning, storage and distribution options on those costs. For the Office of Hydrogen, Fuel Cells and Infrastructure Technologies (OHFCIT) this project has developed a model of hydrogen delivery systems to quantify those costs and permit analyses of alternative technologies and operating strategies. This work has been conducted collaboratively by staff of Argonne National Laboratory, NREL and PNNL with the advice and assistance of several industrial partners. Regular interaction has also occurred with OHFCIT’s Fuel Pathways and Delivery Tech Teams.

Tasks completed through June of FY 2009 have been discussed above. The following tasks will be completed by the end of FY 2009:

- The 2.1 point release of HDSAM will be completed and posted on the DOE Web site, along with a revised Users’ Guide.
- In the 2.1 point release, HDSAM’s capabilities will be further expanded. In addition to the expansions discussed above, V 2.1 will include a revised refueling station footprint, an additional cryo-compressed pathway, centralized production, and delivery to multiple urban areas.
- Continued interaction and collaboration among the project partners and with the Fuel Pathways Integration Tech Team, the Delivery Tech Team, and the broader hydrogen modeling community.

FY 2009 Publications/Presentations

1. Mintz, M. and A. Elgowainy, *Reducing the Cost of Hydrogen Fueling: Insights from Delivery Modeling*, National Hydrogen Association Annual Meeting, Columbia, SC, April 2, 2009.
2. Elgowainy, A., *Analysis of Hydrogen Dispensing Options Using HDSAM 2.0*, HIA/IEA Task Definition Workshop, Amsterdam, February 13, 2009.
3. Mintz, M., A. Elgowainy and M. Gardiner, *Rethinking Hydrogen Fueling: Insights from Delivery Modeling*, 88th Annual Meeting of the Transportation Research Board, Washington, D.C., January 14, 2009.

III.2 H2A Delivery Components Model

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Project Start Date: Fiscal Year 2004

Project End Date: September 2009

- Developed short guide to the Delivery Components Model.
- Enhanced the capability of the Delivery Components Model by creating an automation code to allow for multiple runs.
- Created a delivery cost database for the Hydrogen Deployment System Modeling Environment (HyDS-ME).
- Designed six pilot rail delivery components for the Delivery Components Model.
- Developed hydrogen delivery scenarios for customized hydrogen co-production sites.
- Analyzed hydrogen city-wide storage and delivery dynamics for the city of Los Angeles.

Objectives

- Update and maintain the H2A Delivery Components Model.
- Support other models and analysis that include delivery costs.
- Expand the H2A Delivery Components Model by designing new delivery components.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Delivery and System Analysis sections of the Hydrogen, Fuel Cells and Infrastructure Technologies Program (HFCIT) Multi-Year Research, Development and Demonstration Plan:

- (C) Lack of Hydrogen/Carrier and Infrastructure Option Analysis (Delivery)
- (A) Future Market Behavior (Systems Analysis)

Technical Targets

This project is aiming to improve the efficiency of the hydrogen delivery process through analyzing various delivery pathways to understand the behavior and drivers of the fuel and vehicle markets and to meet Milestone 12 from HFCIT Multi-Year Research, Development and Demonstration Plan: “By 2017, reduce the cost of hydrogen delivery from the point of production to the point of use at refueling sites to less than \$1 per kg.”

Accomplishments

- Reviewed the H2A Delivery Components Model v. 2.0.

Introduction

The H2A Delivery Components Model is an Excel-based, publicly available tool that calculates the cost of delivering hydrogen through multiple delivery pathways. The Delivery Components Model is part of a larger set of H2A or “Hydrogen Analysis” models, including the H2A Production Model, H2A Power Model, and the H2A Delivery Scenario Analysis Model (HDSAM). The Production Model calculates the cost of producing hydrogen from a variety of feedstock types and the Power Model calculates the cost of producing hydrogen from stationary fuel cells systems in combined heat, hydrogen, and power applications. HDSAM, developed at Argonne National Laboratory, allows the end-user to choose between multiple delivery pathways to calculate total scenario costs. The H2A Delivery Components Model also calculates delivery costs but provides the end-user with significant flexibility in determining the costs of distinct delivery components, setting unique values for key parameters and constructing customized scenarios. The Delivery Components Model also serves as a tool for generating input delivery cost data for use in other hydrogen models, such as HyDS-ME, HyDRA, and the H2A Power Model.

Approach

To achieve the project objectives, several improvements to the model have been and continue to be made in collaboration with our partners. A variety of delivery options, as well as refueling station sizes, geographic locations and resource availability are being analyzed. In general, the approach to meeting the project goals is to explore multiple potential pathways to determine promising and economical hydrogen delivery options.

Results

Pursuing the project objectives, a significant effort has been made to review a new version of the Delivery Components Model. In the process of this review, several errors were fixed, the model was debugged, and a review report was provided to DOE. During the past year, the model was maintained by updating supporting cost data tables, which are included in the model. Also, a Short Guide to the Delivery Components Model was written to help users understand the types of capital costs included in each delivery component.

In supporting other models and analysis areas, an automation code was created to provide the ability to run the model multiple times using multiple sets of parameters. This capability is especially important for creating large sets of delivery cost data, such as a database to be used by other hydrogen models. The automation code has been used to create a draft of a hydrogen delivery cost database for use in HyDS-ME. The database was used to support two HyDS-ME scenario studies: a Notional California Case Study [2A] and a regional least-cost optimization study of hydrogen delivered to major urban areas from wind farms [3A].

New rail delivery options have been designed within the Delivery Components Model framework. Rail pathways appear to be a low-cost option when large volumes of hydrogen are delivered from remote locations to large cities. In particular, some renewable hydrogen pathways may involve renewable resources distant from large demand centers. Six pilot rail components have been designed as a first draft toward creating rail delivery pathways. They include gaseous and liquid production site terminals, rail transport in rail cars and rail tankers, and city gate terminals for both gaseous and liquid hydrogen. At the production site terminal, hydrogen is loaded into rail cars (or tankers). Every day a single train leaves the production site terminal with a sufficient supply of hydrogen to meet city demand for a number of days equal to the one-way train travelling time. At the city gate terminal hydrogen is reloaded from the rail cars to trucks, which deliver hydrogen to the end consumer. Whenever possible, the H2A default sizes have been preserved in designing both types of terminals. Figure 1 demonstrates the lowest delivery cost regions for delivery to refueling stations requiring 1,000 kg H₂/day. Liquid hydrogen rail delivery is the lowest cost option across a quite large range of demands and distances, becoming the most economical for the large demands and long distances between the production site and the city. As indicated in the figure, gaseous hydrogen rail delivery is the lowest cost option among other delivery options for relatively small demands and moderate distances.

The H2A Delivery Components Model was used to develop hydrogen delivery scenarios from a combined heat, hydrogen, and power (CHHP) facility to a refueling

FIGURE 1. Least-cost hydrogen delivery map. Refueling station capacity is 1,000 kg H₂/day. (GH2 – gaseous hydrogen, LH2 – liquid hydrogen)

station (either a public retail station or a fleet refueling station) and to calculate the total delivery cost. In this study generic CHHP delivery scenarios with unique cost assumptions have been analyzed and compared with the scenarios using the H2A default input parameters. Figure 2 shows the total hydrogen delivery cost for one of the generic scenarios called “Onsite Fueling.” The jump in cost at the 250 kg/day station capacity is due to an increased compressor capital cost for the flow rates above 250 kg/day. In this case, the refueling station is located at the CHHP site. A short distribution pipeline of 150 ft connects the building where the CHHP system is installed with the refueling station. The pipeline capital costs, operations and maintenance, compressor, and refueling station do not include land costs. Only two compressors are installed at both the CHHP site and the refueling station; and one of each pair is assumed to be working at any time. Friday and summer demand surges are 10% and 8%, respectively. This scenario might apply to facilities with their own land for refueling station equipment. Potential examples of such facilities include supermarkets, airports, university campuses, etc.

City-wide delivery dynamics have been analyzed for the city of Los Angeles. Variations in station sizes across the city area and their evolution over the period 2012-2050 have been taken into consideration. The station size distribution model discussed in [1B] was applied. All refueling stations in the city were divided into three clusters: big (10%), average (30%), and small (60%). Three rates of market growth (scenarios) were considered. Hydrogen was assumed to be produced via steam methane reformer (SMR) technology either at the central production plant or at the forecourt station. Figure 3 shows the station size distribution for all three clusters over the years in one of these scenarios. The costs of delivered hydrogen with respect to station size and types of production and delivery are shown in Figure 4.

FIGURE 2. Hydrogen Delivery Cost – CHHP Onsite Refueling Scenario

FIGURE 3. Refueling station size distribution in Los Angeles. Distribution sizes divided into three major clusters: big, average, and small. The figure shows the average station size in a cluster.

Conclusions and Future Directions

In FY 2009 the Components Model was reviewed and updated. The major goals that have been reached are the following:

- The automation code for the Delivery Components Model was created.
- Large sets of the delivery cost data were obtained for input in other hydrogen models.
- New pilot rail hydrogen delivery options were designed.
- Delivery scenarios from the CHHP sites were developed and analyzed.
- Spread in station sizes and their costs in the city of Los Angeles were studied.

FIGURE 4. Hydrogen delivered cost in Los Angeles. Cost depends on production and delivery pathways, as well as on refueling station size distribution throughout the city. The markers on the graph represent the following: big diamonds - big station cluster, squares - average station cluster, dotted line - small station cluster, bold line - volume-weighted average.

In the upcoming year, the major effort for the Delivery Components Model will focus on:

- Adding a high pressure (700 bar) gaseous refueling station option.
- Adding an option to dispense gaseous hydrogen via cascade system or booster compressor.
- Adding liquid cryo-compressed refueling station.
- Expanding and finalizing the delivery cost database.
- Refining delivery scenarios for CHHP systems.
- Continuing the development of rail delivery components.
- Adding renewable production technologies to the analysis of Los Angeles station distribution scenarios.

FY 2009 Publications/Presentations

1A. O. Sozinova, Delivery Analysis: Milestone Report (2.7.1) and Deliverable (2.7.1), December 2008.

2A. B. Bush, M. Melaina, O. Sozinova, D. Thompson, "Hydrogen Deployment System Modeling Environment: Notional California Case Study," National Renewable Energy Laboratory, January 2009.

3A. B. Bush, M. Melaina, O. Sozinova, "Optimal Regional Layout of Least-Cost Hydrogen Infrastructure," poster presentation at the National Hydrogen Association Conference, Columbia, South Carolina, March 30 to April 3, 2009.

4A. O. Sozinova, "Rail and Pipeline Networks as New Hydrogen Delivery Options," Delivery Tech Team Meeting, Cambridge, MD, April 17, 2009.

- 5A.** O. Sozinova, “H2A Delivery Components Model,” Annual Merit Review, Arlington, VA, May 21, 2009.
- 6A.** O. Sozinova, “Rail Components and Hydrogen Delivery Networks,” H2A Meeting, Arlington, VA, May 18, 2009.

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- 1B.** M. Melaina, J. Bremson, “Regularities in Early Hydrogen Station Size Distributions,” Conference of the United States Association of Energy Economics, Ann Arbor, Michigan, September 24–27, 2006.

III.3 Hydrogen Regional Infrastructure Program in Pennsylvania*

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Contract Number: DE-FC36-04GO14229

Subcontractors:

- Air Products and Chemicals, Inc., Allentown, PA
- Resource Dynamics Corporation, Vienna, VA

Start Date: September 1, 2004

Projected End Date: July 31, 2009

*Congressionally directed project

Objectives

Analysis of Hydrogen Energy Stations for Initial Hydrogen Infrastructure in Northeastern States along the I-95 Corridor

- Assess the feasibility of a hydrogen infrastructure based on the concept of hydrogen energy stations along the northeastern I-95 corridor states.

Hydrogen Sensors

- Advance current hydrogen-specific sensors and sensor technologies to ensure reliable operation and performance in hydrogen applications.

Technical Barriers

This project was executed to address the following technical barriers from the Hydrogen Delivery section (3.2.4) [1] of the DOE's Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan (MYRDDP):

- (A) Lack of Hydrogen/Carrier and Infrastructure Options Analysis

(K) Safety, Codes and Standards, Permitting

(I) Hydrogen Leakage and Sensors

(J) Other Refueling Site/Terminal Operations

Technical Targets

The Hydrogen Regional Infrastructure Program in Pennsylvania project was established to conduct research in multiple areas. Insights gained from these studies are being used to address the following technical targets detailed in the Hydrogen Delivery section of the MYRD&DP:

Hydrogen Energy Stations for Initial Hydrogen Infrastructure in Northeastern States along the I-95 Corridor

- DOE's 2015 target of \$2.00–\$3.00/gge (delivered, untaxed) at the pump for hydrogen

Hydrogen Sensors

- Hydrogen leakage (% of hydrogen leakage from pipeline): <0.5% (2017)

Accomplishments

The following items are accomplishments to date for the Hydrogen Regional Infrastructure Program in Pennsylvania project:

Analysis of Hydrogen Energy Stations for Initial Hydrogen Infrastructure in Northeastern States along the I-95 Corridor

- Analyzed using lighthouse projects that could serve as an anchor for various hydrogen fueling stations. Focused on hydrogen energy stations, landfill gas and anaerobic digestion gas, and coke oven gas.
- Gathered site-specific and state-specific data, including actual costs for natural gas and electricity.

Hydrogen Sensors

- Achieved successful integration of the hydrogen sensor into a complete sensor package.

Section 1. Pennsylvania Hydrogen Delivery and the I-95 Corridor

Introduction

Hydrogen is expensive to produce and distribute in small volumes, relative to gasoline costs. Phase II work showed that for the 1 percent demand scenario, the

costs required to produce and deliver hydrogen from a central plant were over \$9/kg. Distributed production produces hydrogen in smaller quantities with natural gas directly at the fueling stations, and avoids the costs of delivery. Using this method, hydrogen costs were lower, around \$7/kg (Figure 1). These costs are significantly higher than the DOE goal of \$3/kg, and current gasoline prices. Eventually, as demand builds to more modest levels, delivered costs approach the \$3/kg DOE goal and compare with current gasoline prices.

The I-95 corridor from Washington, DC to Boston, Massachusetts is an important market for hydrogen and hydrogen analysis because it contains 10 closely-tied metropolitan statistical areas (MSAs)¹, with four of the nation's largest cities, as well as a variety of potential feedstocks and delivery infrastructures. This places an importance on establishing hydrogen infrastructure within this key transportation corridor as it is reflective of many of the challenges the nation faces in moving towards a hydrogen economy.

Approach

The analysis of hydrogen energy stations (HESs) illustrates the benefits of investing in infrastructure that serves a dual purpose, providing heat and power to its host site while also furnishing a modest amount of hydrogen for refueling purposes.

Results

The results of the analysis show that investment in HESs (Figure 1, Tables 1, 2, 3 and 4), in part due to existing state and federal incentives, can provide attractive return on investment in states such as New Jersey and Connecticut, and provide lighthouse projects upon which the I-95 hydrogen economy can be grown. Similar incentives may be needed in other states, to provide a clustering of refueling sites, until hydrogen demand can be built high enough to attract dedicated hydrogen refueling and lower production and delivery costs are realized with increased demand scenarios and combined MSAs.

The states with the most attractive economics for renewable gas (biogas from landfills and wastewater treatment plants) and natural gas-based HES applications along the I-95 Corridor are Connecticut, New Jersey, New York and Pennsylvania. All of these states contain numerous sites in close proximity to the I-95 Corridor. With these HES installations at strategic locations in these states, a hydrogen economy with vehicle refueling stations would begin to emerge.

¹ From South to North: Washington, D.C., Baltimore, Philadelphia, Trenton, New York, Bridgeport, New Haven, Hartford, Providence, and Boston

FIGURE 1. Cost of Producing Hydrogen with HES for Prevailing Electricity and Natural Gas Costs

While the HES 300 is seen as a good starting point for potential HES projects, the larger HES 1500 and HES 1600 systems provide better economics under current market conditions, provided that all of the heat and power can be utilized on-site. Several states have sites that are offering estimated payback periods of shorter than three years, with most sites offering paybacks in the 3–4 year range, for the renewable HES. However, only Connecticut and New York show three-year payback potential for the natural-gas HES, with all industrial sectors in Connecticut having payback periods less than three years.

Table 4 provides results from the various sites that were used as case studies, and suggests ways to improve project economics. For the case studies, only the HES 300 and HES 1500 are considered, as these options reflect HES that have been engineered as a system. While this analysis confirms that sites with positive economics are available, those with attractive (less than three-year payback) economics are not so easily found, but do exist.

There are four of the 19 active domestic coke plants in Western Pennsylvania near Pittsburgh. The waste gas streams from these coke ovens provide not only the most cost-effective, but also the most environmentally-green feedstock for hydrogen production. This production pathway would be the most likely to witness beneficial results for a hydrogen economy in the near-term. The price differential between hydrogen and natural gas offers enough financial benefits to coke producers to make the entire stock available for hydrogen production as long as there are sufficient market demands. This region shows a huge potential for a wide-spread deployment of hydrogen-powered fuel cells for light-duty vehicles and power generation stations and is well-positioned to benefit from the readily accessible coke plants.

TABLE 1. Hydrogen Energy Station Configurations

HES Configuration	HES 300	HES 1500	HES 400	HES 1600
Fuel Cell Module	DFC 300	DFC 1500	Purcell 400	4 x Purecell 400
Electrical output (kW)	300	1350	380	1520
Hydrogen output (kg/day)	125	125	27	108
Thermal output (kW)	75	300	480	1900
Notes	Employs a custom-designed hydrogen purification unit developed by Air Products. Electrical, thermal and hydrogen output provided by Fuel Cell Energy.		Employs an off-the-shelf hydrogen purification unit developed by H2Gen. Thermal and hydrogen output estimated by RDC from product literature based on 5 percent of reformer output diverted from fuel cell.	

TABLE 2. Number of Sites Capable of Supporting Renewable HES Projects, by State and Estimated Payback Period

City/State	Payback < 3 Years	Payback 3–5 years	Payback 5–7 years	Total
Connecticut	6	1	3	10
Washington, DC	1	0	0	1
Boston, MA	0	0	1	1
New Jersey	2	16	2	20
New York, NY	11	6	0	17
Philadelphia, PA	3	1	0	4

TABLE 3. Number of Sites Capable of Supporting Natural Gas HES Projects, by State and Estimated Payback Period

City/State	< 3 Years	3–5 Years	5–7 Years	Total Potential NG Sites
Connecticut	900	10,474	722	12,096
Washington, DC	0	0	80	80
Boston, MA	0	0	0	0
New Jersey	0	0	2,450	2,450
New York, NY	0	57	11,574	11,631
Philadelphia, PA	0	0	3,253	3,253

Conclusions and Future Directions

While the prospects for HES in D.C. and Boston do not look promising with current price and performance estimates and market conditions, there appears to be a great deal of potential on the I-95 Corridor from Philadelphia through New Jersey, New York, and Connecticut. The keys are targeting the large renewable sites (landfills and wastewater treatment plants), manufacturing facilities, hospitals, and other commercial

sites with positive HES economics along the I-95 Corridor, and identifying uses for the hydrogen produced that will procure hydrogen at the rate of \$7/kg. This may include distribution centers with battery-powered forklifts that can be converted to fuel cell-powered units, sales contracts with industrial facilities, or hydrogen refueling stations for fuel cell vehicles. In a developing hydrogen economy, HESs could play a crucial role in implementing an early infrastructure of refueling stations for light duty fuel cell vehicles along the I-95 Corridor.

TABLE 4. HES Case Studies of Individual Sites along the I-95 Corridor

State	Site	HES Option	Est. Payback Period (Yrs.)	Areas to Improve Payback
CT	Hospital	HES 1500	2.4	The 2008 natural gas costs used in the analysis are relatively high – lower costs would lower the payback period.
CT	Travel Center	HES 300	5.3	Facility averages about 180 kW, while HES output is 250 kW – in an average hour, 180 kWh replaces high-price electricity, while 70 kWh is sold at utility's avoided cost – economics improve for larger facilities.
DE	Big Box Distribution Center	HES 1500	8.2	Delaware currently offers no state incentive – a \$1 million incentive would lower payback by almost 2 years. Also, little/no thermal demand in summer months.
NJ	Distribution Center	HES 300	9.6	Thermal load is nonexistent in summer months, so excess thermal energy must be dumped – finding an outlet for this energy would improve project economics.
NJ	Hospital Complex	HES 1500	7.2	Electricity and natural gas prices were typical for New Jersey – RECs or other incentives for natural gas fuel cells would help economics.
NJ	Rutgers EcoComplex LFG	HES 300	7.8	LFG availability only 85 percent; facility is too small for HES 300 base load operation, so excess electricity is sold through net metering at the avoided cost rate – a larger facility with more accessible LFG would obtain a better payback.
NY	Big Box Distribution Center	HES 1500	5.4	Little to no thermal demand during the summer months – if excess thermal energy could be utilized, project economics would improve.
		HES 1500 with Fuel Cell Forklifts	3.6	Incorporating the forklift investment to convert fleet to fuel cells creates on-site demand for hydrogen, and improves payback for combined investment. Investment includes additional hydrogen purification.
PA	Grocery Distribution Center	HES 300	18.6	Low electricity prices, high natural gas prices, and low summer thermal demand prevent this site from achieving a desirable payback period.

RECs - renewable energy credits

LFG - landfill gas

To facilitate the early adoption of HESs, the DOE should consider a two-pronged approach. First, there are a number of potential sites in the New York and Connecticut areas that could deploy HES technology economically. Work would have to be done to locate these sites and find a host for the hydrogen output. Potential options other than a vehicle refueling station include distribution centers that could convert to fuel cell forklifts, and industrial or institutional purchasers of hydrogen. Secondly, many of the sites contacted in this project were unaware of HESs and even of the developmental status of stationary fuel cells in general. To accomplish heightened awareness, an educational campaign could also be launched in concert with the states along the I-95 Corridor to provide factual

information about fuel cells as well as a vision for the hydrogen economy. Addressing both of these recommendations would remove some of the key barriers to HES adoption, as well as those impeding a hydrogen infrastructure in general.

Since Pittsburgh is strategically located near four major coke plants, it is recommended that a multi-year feasibility study and demonstration project be pursued at the DTE Shenango coke battery to verify and validate the concept and cost benefits as well as to identify and solve any technical problems associated with practical application of the coke oven gas-to-hydrogen production process.

Section 2. Hydrogen Sensors

Introduction

The objective of the Phase III sensor work was to develop and fabricate a hydrogen sensor unit and install the unit at a hydrogen refueling station. The sensor technology and manufacturer used during the Phase III work was selected previously during the Phase II portion of this project. The hydrogen sensor unit developed also included remote monitoring capabilities. Testing and operation of a completed unit was also included in Phase III.

Approach

During Phase I and Phase II of the Hydrogen Regional Infrastructure Program in Pennsylvania, sensor technology A was selected as the optimum technology to be used in creating a complete H₂ sensor unit in Phase III. As part of Phase III, an actual hydrogen sensor unit was designed and assembled.

Results

Based on the results and work conducted as part of Phases I and II, sensor technology A was selected to be used in Phase III to develop and test a hydrogen sensor unit. This technology was selected for the following reasons:

- The sensor has had at least five years of development, and the microelectronic manufacturing process steps have been well developed in producing other types of sensors by the manufacturer.
- Testing results showed that the sensor had the highest speed of response of all the sensors tested. Fast response time leads to innovative applications.
- Testing results showed that the sensor had no detectable interferences from components found in natural gas systems.
- Of the available palladium-based sensors, this sensor had the lowest power requirements. The benefit is the impact on power sourcing requirements and promotes innovative applications.

During the Phase III efforts, the hydrogen sensor unit was developed and fabricated at an affiliate of Air Products' located in New Mexico. Following the assembly, the unit was laboratory-tested at the manufacturing location and then shipped to Air Products' facility in Allentown, Pennsylvania where further laboratory testing was conducted. The purpose of the laboratory testing was to ensure the unit was operating as expected.

The results of the testing showed that the sensor unit possesses hydrogen-specific response (<0.0500% to >4.000% H₂), no other molecular interferences, high speed response (<0.5 second), wireless (1 mile) and internet protocol communications, and has designed-in adaptability for future expansions such as an internal self-test specific for hydrogen (unique to this system). The results of the laboratory testing were satisfactory and showed the unit was operating as expected. Following this testing, the units were installed at a shuttle bus refueling station that is located on Air Products' Campus in Allentown, Pennsylvania.

Conclusions and Future Directions

The sensors work was completed at the end of Phase III for this project. It is expected that the unit will be operated and tested at this refueling station during a future project.

FY 2009 Publications and Presentations

1. Eileen M. Schmura, Paul L. Lemar, Jr and Sarah Largent, *Northeastern I-95 Corridor and Pennsylvania Indigenous Energy*, NHA Annual Hydrogen Conference 2009, Columbia, SC, (April 2009).
2. Paul L. Lemar Jr. and Eileen Schmura, *Building a Transitional Hydrogen Infrastructure Using Warehouses as Lighthouse Projects*, NHA Annual Hydrogen Conference 2009, Columbia, SC (April 2009).
3. Kevin L. Klug, *The Department of Energy's Pipeline Working Group Round Robin Test Program*, 2008 International Hydrogen Conference, Wyoming, (September 2008).
4. Vladimir M. Shkolnikov, *Fatigue Performance of Composite Overwrapped Pressure Vessels*, NHA Annual Hydrogen Conference 2009, Columbia, SC (April 2009).

References

1. DOE, "Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan," April 27th, 2007.

III.4 Oil-Free Centrifugal Hydrogen Compression Technology Demonstration

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Contract Number: DE-FG36-08GO18060

Subcontractor:

Mitsubishi Heavy Industries, Ltd, Hiroshima, Japan

Project Start Date: September 25, 2008

Project End Date: August 31, 2011

Objectives

Demonstrate key technologies needed to develop reliable and cost-effective centrifugal compressors for hydrogen transport and delivery:

- Eliminate sources of oil/lubricant contamination.
- Increase efficiency by using high rotational speeds.
- Reduce system cost and increase reliability.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Delivery section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (B) Reliability and Costs of Hydrogen Compression
- (I) Hydrogen Leakage and Sensors

Technical Targets

This project is directed towards the design, fabrication and demonstration of oil-free centrifugal compression technology. This project will identify the key technological challenges for development of a full-scale hydrogen/natural gas centrifugal compressor. The project addresses the DOE technical targets from the Hydrogen Delivery section of the Hydrogen, Fuel Cells and

Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan (see Table 1).

TABLE 1. Technical Targets for Hydrogen Compression

Category	2005 Status	FY2012	FY2017
Reliability	Low	Improved	High
Energy Efficiency	98%	98%	> 98%
Capital Investment (1M) (based on 200,000 kg of H ₂ /day)	\$15	\$12	\$9
Maintenance (% of Total Capital Investment)	10	7	3
Contamination	Varies by Design		None

Accomplishments

- Reviewed design requirements for compression of hydrogen with a flow of 500,000 to 1,000,000 kg/day with an output pressure of 1,200 psig.
- Completed preliminary compressor design with seven compression stages and established the impeller diameter and the desired rotational speeds.
- Conducted stress analysis to determine the range of stresses developed in the rotor for several selected materials.
- Conducted rotor dynamic analysis to ensure dynamic stability of the rotor design.

Introduction

One of the key elements in realizing the hydrogen economy is the deployment of a safe, efficient hydrogen production and delivery infrastructure on a scale that can compete economically with current fuels. The challenge, however, is that hydrogen, lightest and smallest of gases with a lower viscosity than natural gas, readily migrates through small spaces. While efficient and cost-effective compression technology is crucial to effective pipeline delivery of hydrogen, today's positive displacement hydrogen compression technology is very costly, has poor reliability and durability, especially for components subjected to wear (e.g., valves, rider bands and piston rings). Even so called "oil-free" machines use oil lubricants that migrate into and contaminate the gas path. Due to the poor reliability of compressors, current hydrogen producers often install duplicate units in order to maintain on-line times of 98-99%. Such machine redundancy adds substantially to system capital costs. Additionally, current hydrogen compression often

requires energy well in excess of the DOE 2% goal. As such, low capital cost, reliable, efficient and oil-free advanced compressor technologies are needed.

Approach

The MiTi team will meet project objectives by conducting compressor, bearing and seal design studies; selecting components for validation testing; fabricating the selected centrifugal compressor stage and the corresponding oil-free bearings and seals; and conducting testing of the high-speed, full-scale centrifugal compressor stage and oil-free compliant foil bearings and seals under realistic pressures and flows in a hydrogen gas environment. Specific tasks include: (1) preliminary oil-free, multi-stage, high-speed centrifugal compressor system design; (2) detailed design of a full-scale centrifugal compressor stage; (3) mechanical component detailed design of the oil-free bearings, seals and shaft system needed to test the compressor stage; (4) test hardware fabrication; (5) dynamic test; (6) compressor performance test; (7) system design refinement; and (8) project management and reporting.

Results

A preliminary compressor design study was performed using commercial aerodynamic performance software. The accuracy of this software's performance predictions was first validated with published data from a commercially available compressor wheel. The design software was able to predict the performance over a wide range of speed and flows with errors of 3%. Results were further validated by using MiTi's own in-house compressor performance code.

The parametric study began with a detailed analysis of a single compression stage that would then form the basis for the multi-stage frames. The proposed compressor design uses a double entry design so that each impeller is only required to compress 250,000 kg/day, or half of the total projected flow, to achieve the required 700 psig pressure rise. In order to achieve the required 700 psig pressure rise with six or seven stages of compression, each stage will need to have a pressure ratio between 1.13 to 1.15. The exact pressure ratio required per stage will be determined through iterative analysis with results from single stage predictions and other details of the system design, including factors such as seal losses and effectiveness of intercooling. Based upon several preliminary single stage design iterations, the baseline nominal impeller stage size was selected for use in the parametric analysis. The single stage parametric study was then performed with six different compressor diameters at seven different operating tip speed conditions while maintaining the hydrogen inlet conditions fixed as noted below:

Fluid: Hydrogen Gas

Inlet Flow: 382 lb/min (250,000 kg/day)

Inlet Temperature: 68°F

Inlet Pressure: 500 psig

Using the fixed hydrogen inlet conditions, the first compressor stage performance was predicted at tip speeds of 1,200-1,800 ft/s. For this tradeoff and preliminary design study, each stage consisted of the impeller, crossover and return channel. Each tradeoff design point evaluated was optimized for the imposed tip speed and geometry conditions. This approach was chosen to permit a direct comparison of stage efficiencies between each design configuration. In Figure 1, the results indicate that for all impeller diameters analyzed, the desired stage pressure ratio of at least 1.13 is obtained at a compressor impeller tip speed of 1,500 ft/s or higher. While the different scaled impeller diameters show very similar predicted pressure ratios at speeds above 1,400 ft/s, the predicted efficiencies and power requirements, as seen in Figures 2 and 3, show a clear benefit of using the full-scale impellers as well as those scaled up as much as 25%. Conversely, the 90% and 80% scaled diameters demonstrate considerably lower efficiency and higher power requirements.

Having confirmed the validity of the full-scale impeller design through the tradeoff study, it was then used in the investigation in the multi-stage performance at an impeller tip speed of 1,500 fps. The selected double entry design was used for the preliminary multi-stage analysis. In earlier analyses, MiTi identified that a limit of three stages of compression (i.e., six single stage impellers) on a single shaft should be imposed in order to obtain suitable rotor-bearing system dynamic performance while also providing for enhanced intercooling options and modular assemblies. Therefore, the double entry 3-stage machine was modeled as two

FIGURE 1. Pressure Ratio as a Function of Tip Speed and Impeller Size

FIGURE 2. Adiabatic Efficiency as a Function of Tip Speed and Impeller Size

FIGURE 3. Gas Power as a Function of Tip Speed And Impeller Size

separate 3-stage machines, each compressing half of the total hydrogen inlet flow of 250,000 kg/day. The desired pressure rise of 217 psig was achieved at a polytropic efficiency of 74% and would require input power of approximately 2,430 HP for the three stages (or a total of 4,860 HP for the entire frame).

The multi-stage frame was further investigated for the possible benefits of placing intercoolers between stages 1 and 2 and 2 and 3. The addition of intercoolers reduced the power required in stage 2 by 5% and stage 3 by 9%. Despite the small pressure drop experienced with intercoolers, the reduced power demand warrants their inclusion in the system. It was also observed that the use of intercoolers would make it easier to match performance between stages and, thus, contribute to higher overall system performance.

Finite element analysis was used to evaluate the stress distribution of the rotor design selected for the

compressor. Four different materials with a wide range of elastic properties and strengths were selected and evaluated in this analysis. In addition, certain aspects of the design were varied in the analysis to evaluate the effects of geometric design on the stress distribution. In the analysis, a rotational speed of 60,000 rpm, which corresponds to a tip speed of nearly 1,800 ft/s, was used.

The stress analysis was performed following mesh generation and assigning appropriate boundary conditions. One end of the shaft was assumed to be fixed and the rotational speed of 60,000 rpm was applied to the entire body as an internal load. Therefore, only centrifugal stress was considered. The analysis was performed for a high strength stainless steel, high strength aluminum alloy, a titanium alloy and high strength steel. The overall von Mises stress distribution, the distribution in the cross section and the distribution on one of the rotor disks are shown in Figure 4 for one of the materials. The analysis confirmed that the stress concentration on the backside of the disk could be greatly improved by modifying the transition radius. These results and similar future analyses will be used to down select the rotor material and the specific geometric design for the rotor.

The analyses performed for stress distribution in pure rotation was extended by the addition of a rotational torque. In addition to the rotational speed of 60,000 rpm, a torque corresponding to 5,500 HP at 60,000 rpm was applied to the free end of the rotor. In this analysis both the centrifugal and torsional stresses were analyzed. The stress distribution, however, remained about the same as those without the torque.

Rotor dynamic analysis was performed on the selected rotor geometry to determine the speed at which the first critical bend occurs. The model is shown in Figure 5 where the unbalanced forces were included to match the rotor responses at two sensor locations measured from previous experiments. The predicted rotor response at the sensor locations and the bending moments at the bearing locations are shown in Figure 6 for one of the analyses. The analysis predicted that, in this case, the first critical bend would occur at about 35,000 rpm. The finite element model was modified by adding two grounded springs attached to the shaft at each bearing location to constrain the two perpendicular radial directions instead of fixing the shaft at one end. Appropriate bearing stiffness values were assigned as the spring constants and the bending moments at the first bending critical speed from the rotor dynamic analysis were applied to the shaft at the two bearing locations. The analysis was performed for a rotational speed of 60,000 rpm. Therefore, in this analysis both the centrifugal and bending stresses were included. The results indicated that the effect of adding the bending moment was insignificant and the stress values remained practically unchanged. Therefore, it is concluded that

FIGURE 4. Typical Stress Distribution in the Rotor due to Rotation: (a) Surface Stresses, (b) Cross-Section, and (c) Cross-Section in one Disk.

the torque and bending moments are carried by the core shaft only and have no effect on the disks, which mainly carry the centrifugal stress.

Conclusions and Future Directions

The design requirements for compression of hydrogen with a flow of 500,000 to 1,000,000 kg/day with an output pressure of 1,200 psig were reviewed. A preliminary compressor design with seven compression stages was completed. The impeller diameter and the desired rotational speeds were established. Stress analysis was conducted to determine the range of stresses developed in the rotor for several selected materials. It was concluded that the addition

FIGURE 5. Model of the Rotor for Rotor Dynamic Analysis

FIGURE 6. Predicted Results from the Rotor Dynamic Analysis: (a) Displacements, (b) Moments in one Bearing Location, and (c) Moments in the other Bearing Location.

of torque and bending moments due to passing through the first bending mode are carried by the core shaft only and have no effect on the disks, which mainly carry the centrifugal stress. The following tasks are planned for the remainder of Fiscal Years 2009 and 2010:

- Refine multi-stage/multi-frame compressor concept
- Select one stage for detailed design and test
- Conduct preliminary design review with DOE
- Conduct detailed design

FY 2009 Publications/Presentations

1. “Oil-Free Compression for Hydrogen Delivery and Transportation,” Hydrogen Delivery Technology Team Meeting, August 2008, Columbia, MD.
2. “Oil-Free Centrifugal Hydrogen Compression Technology Demonstration,” DOE Hydrogen Program Annual Review and Peer Evaluation Meeting, May 2009, Arlington, VA.

III.5 Development of a Centrifugal Hydrogen Pipeline Gas Compressor

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Contract Number: DE-FG36-08GO18059

Subcontractors:

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- Texas A&M University, College Station, TX
- HyGen Industries, Eureka, CA

Project Start Date: June 1, 2008

Project End Date: July 30, 2011

Objectives

Develop and demonstrate an advanced centrifugal compressor system for high pressure hydrogen pipeline transport to support DOE's Strategic Hydrogen Economy Infrastructure Plan:

- Delivering 100,000 to 1,000,000 kg/day of 99.99% hydrogen gas from generation site(s) to forecourt stations.
- Compressing from 350 psig to 1,000 psig or greater.

Reduce initial installed system equipment cost to less than \$9M (for a compressor package of \$5.4M for 200,000 kg/day (note: \$6.2M for a 240,000 kg/day) system by Fiscal Year 2017:

- Reduce package footprint and improve packaging design.

Achieve transport delivery costs below \$1/gasoline gallon equivalent (gge):

- Reduce maintenance cost to below 3% of total installed cost by FY 2017.
- Increase system reliability thus avoiding purchase of redundant systems.
- Maintain hydrogen efficiency (as defined by DOE) to 98% or greater.

- Reduce H₂ leakage to less than 0.5% by FY 2017.

Technical Barriers

This project addresses the following technical barriers from the Delivery section of the **“Hydrogen, Fuel Cells, and Infrastructure Technologies Program Multi-Year Research, Development, and Demonstration Plan”** [1]:

(B) Reliability and Costs of Hydrogen Compression

Technical Targets

The project has met the DOE Targets as presented in DOE's **“2007 Technical Plan for Hydrogen Delivery”** Projects (Table 1).

TABLE 1. Progress Towards Meeting Technical Targets for Delivery of Hydrogen via Centrifugal Pipeline Compression

Characteristic	Units	DOE Target	Project Accomplishment
Hydrogen Efficiency (f)	[btu/btu]	98%	98%
Hyd. Capacity (g)	kg/day	100,000 to 1,000,000	240,000
Hyd. Leakage (d)	%	<0.5	0.2 (goal)
Hyd. Purity (h)	%	99.99	99.99
Discharge Pressure (g)	psig	>1,000	1,200
Comp. Package Cost (g)	\$	6.2	4.5
Main. Cost (Table 3.2.2)	\$/kWhr	0.007	0.005 (goal)
Package Size (g)	sq. ft.	300 to 350	175 to 200
Reliability (e)	# Sys.s Req.d	1 redundant sys. Reduced from 2	Modular sys.s with 240K kg/day with no redundancy req.d

Note: Letters Correspond to DOE's 2007 Technical Plan-Delivery Sec. 3.2 - page 16

Accomplishments

Developed computer models to aid in analysis of hydrogen compressor:

- Performance and Equipment Cost Model
 - Suitable as a macro for DOE “HDSAM v2.0” economics model.
 - Identifies hydrogen compressor package performance and component cost. Over 30 alternative compressor-gearbox configurations, materials, and compressor drive options

(including gas turbine drives with heat recovery for intercooler cooling) studied and evaluated using a Relative Risk and Relative Cost Optimization Program developed for the project culminating in a “best” choice for the compressor package.

- System Reliability and Maintenance Cost Model
 - Estimates comparative reliabilities for piston and centrifugal compressors for pipeline compressors developed.
 - Failure Mode Effects Analysis (FMEA) for component risk and reliability assessment.
 - Estimates operation and maintenance costs for compressor system.

Preliminary design details of pipeline compressor module completed including:

- Compressor design conditions confirmed by project collaborators.
 - $P_{\text{inlet}} = 350$ psig, $P_{\text{outlet}} = 1,200$ psig; flow rate = 240,000 kg/day
- Six-stage, 60,000 revolutions per minute (rpm), 3.33 pressure ratio compressor.
- Integral gearbox pinions driving individual, overhung impellers.
- Design of compressor’s major mechanical elements completed and satisfied by two manufacturers per component:
 - Tilting pad radial and thrust bearings designs validated for use.
 - Two commercially available gas face-seals have been validated for use.
- Heat exchanger specifications met by two manufacturers to cool hydrogen gas to 100°F between stages.
 - Tranter plate-type heat exchanger design.
 - Heatric heat exchanger (compact, plate-fin surface core).

Introduction

The DOE has prepared a Multi-Year Research, Development, and Demonstration Plan to provide hydrogen as a viable fuel for transportation after 2020, in order to reduce the consumption of limited fossil fuels in the transportation industry. Hydrogen fuel can be derived from a variety of renewable energy sources and has a very high energy content per kg, equivalent to the energy content in a gallon of gasoline. The switch to hydrogen-based fuel requires the development of an infrastructure to produce, deliver, store, and refuel

vehicles. The least expensive delivery option for hydrogen involves the pipeline transport of the hydrogen from the production sites to the population centers where the vehicles will see the highest demand, and thus, have the greatest impact on reducing the U.S. dependency on fossil fuel. The cost to deliver the hydrogen resource to the refueling stations will add to the ultimate cost per kg or per gallon equivalent that needs to be charged for the hydrogen fuel. Therefore, it is necessary that the cost to deliver the hydrogen be kept as low as possible, which implies that the cost of the compressor stations, their installation costs, and their efficiency in pumping the hydrogen fuel to the refueling stations must be kept low. DOE has set a target of \$1/gge.

The delivery cost target can be met if the compressor system can be made more reliable (to reduce maintenance costs), more efficient (to reduce operation costs), and be a smaller, more complete, modular package (to reduce the compressor system equipment, shipment, and its installation costs).

Approach

The technical approach used by Concepts NREC to accomplish these goals is to utilize state-of-the-art aerodynamic/structural analyses to develop a high-performance centrifugal compressor system for pipeline service. The centrifugal-type compressor is able to provide high pressure ratios under acceptable material stresses for relatively high capacities -- flow rates that are higher than what a piston compressor can provide. Concepts NREC’s technical approach also includes the decision to utilize commercially available, and thus, proven bearings and seal technology to reduce developmental risk and increase system reliability at a competitive cost. Using its expertise in turbomachinery analysis, design, machining, and testing, Concepts NREC is researching the use of a material that is compatible with hydrogen and that can enable the highest possible impeller tip speeds, reducing the number of required stages while meeting DOE’s goals for overall pressure ratio and efficiency. In order to minimize the development time and ensure industrial acceptance of the design for the new pipeline compressor system, Concepts NREC has assembled a project team that will assist in the advanced engineering of the compressor while also preparing an implementation plan that can provide for near-term industrial pipeline applications.

The engineering challenge to implement this technical approach is to design a compressor stage that can achieve the highest acceptable pressure ratio and thermodynamic efficiency per stage, while also using as few stages as possible and employing the smallest diameter impeller. For centrifugal-type compressors, the pressure ratio is proportional to the square of the rotor speed, rpm², and the radius². Thus, even a small increase

in tip speed or impeller radius results in significant increases in pressure. The aerodynamic design challenge in reducing the number of stages is to maximize tip speed of the centrifugal compressor impeller while staying within acceptable design safety levels of the strength limitations of the material in addition to utilizing advanced diffuser systems to maximize recovery of dynamic head into static pressure. However, material stresses also increase proportionally to the square of the rotor speed (rpm^2) and radius (radius^2), and also by material density. Ultimately, the major constraint is imposed by the limitations of the maximum stress capability of impeller material. This constraint is further aggravated by the need for the material selection to consider the effects of hydrogen embrittlement on the strength of the material.

These engineering challenges are best summarized by their inter-dependencies, as illustrated in Figure 1. As may be observed from Figure 1, high impeller tip speeds will enable high pressure ratios to be attained with fewer stages. Thus, a major challenge for the project was to identify the material that can enable the highest tip speeds to be attained while also sustaining the stresses that are imposed by these tip speeds.

The need for high operating tip speeds is also constrained by the desire to have a small radius impeller, resulting in the adoption of a relatively high operating speed. The need to operate at high speed requires careful consideration of the rotor dynamics of the compressor and high-speed assembly, and the design of an adequate, high-speed ratio gearbox. All of these critical engineering constraints need to be satisfied by employing commercially available components that are operated within the manufacturer's design guidelines

for state-of-the-art materials, loads, stresses, operating speeds, and power ratings.

Concepts NREC has met all of these engineering challenges in order to provide a pipeline compressor system that meets DOE's specifications for near-term deployment.

Results

In order to achieve a packaged pipeline centrifugal compressor-based design that complies with the major engineering constraints imposed by state-of-the art materials and commercially available components, and that satisfies all of the DOE requirements, Concepts NREC has developed several computer design models that would optimize the design choice. These models include:

1. Compressor Package Performance Model that provides a single point summary of each of the components within the package:
 - Compressor rotor aerodynamics (pressure ratio, power, speed vs. flow rate, and intercooler pressure drop).
 - Intercooler size vs. effectiveness (i.e., desired outlet temperature).
 - Electric motor power.
 - Overall hydrogen efficiency based on compressor power and component efficiencies.
 - Compressor shaft diameter sizing based on fatigue loading.
 - Calculation of impeller radial and axial loadings.

FIGURE 1. Engineering Analysis Illustrating Design Dependencies and Constraints

2. Cost Model using algorithms to determine the relative component cost and operational risks associated with compressor design specifications such as:
 - Number of compressor stages, single or back-to-back.
 - Number of volute housings (one or more stages per housing).
 - Rotor rpm.
 - Compressor efficiency.
 - Gearbox (1- or 2-speed step).
 - Driver speed and type.
 - Choice of compressor materials.
 - Rotor materials with or without coatings.
 - Number of intercoolers.
3. Engineering Reliability and Maintenance Cost Model that uses a consistent methodology and algorithms to determine the relative reliability and maintenance cost for a piston and centrifugal compressor pipeline package that:
 - Uses either manufacturers' reliability of individual components or sub-systems that constitute a compressor system (preferred), or textbook values.
 - Uses Federal Energy Regulatory Commission operation and maintenance database as the basis for determining the maintenance costs for a centrifugal compressor.
 - Uses FMEA as developed by Concepts NREC for this project

The Cost and Performance Model enabled the analysis of over 30 combinations of centrifugal compressor impeller speeds, the number of stages, with a single or dual impeller-shaft design using a one or two-step gearbox, with a high or low-speed prime mover drive arrangement. A summary of the options considered is shown in Figure 2. The best choice with respect to conformity to commercially available system

FIGURE 2. A Summary of the Design Selection Process for Choosing an Optimum Arrangement for the Compressor and the Gearbox

specifications and high efficiency and low operational risk is highlighted. This choice is a single, overhung (cantilevered) impeller attached to a drive shaft that includes a shaft seal, bearing, and drive pinion. The impeller rotor is designed without a bored-hub in order to reduce the hub “hoop” stresses. This requires the impeller to be mechanically attached to the high strength steel alloy, a drive shaft with a patented design attachment system that enables the rotor to be removed from the gearbox without removing the drive shaft, and thus, not disturbing the shaft seal and bearings.

The compressor selection uses six stages, each operating at 60,000 rpm with a tip speed of less than 2,100 ft/s. Each compressor, shown in Figure 3, is 8 inches in diameter and has an overall stage efficiency of between 79.5 and 80.5%, for an overall compressor efficiency of 80.3%. A gas face-seal will provide the isolation of the hydrogen from the lubricating oil. The 1,400 hp per stage can be sustained by using two, tilting pad hydrodynamic bearings on either side of a 2.5 inch-long drive-pinion gear. The face seal and bearings are commercially available from Flowserve or Eagle-Burgmann and KMC or Waukesha, respectively. The pinion is part of a custom gearbox manufactured by Cotta Transmission Company and utilizes commercially available gear materials that are subjected to stresses and pitch line speeds that meet acceptable engineering practice.

The material chosen for the compressor is an aluminum alloy. The choice is based on its mechanical strength-to-density ratio or (S_{yield}/ρ) which can be shown to be a characteristic of the material's ability to withstand centrifugal forces. Several grades of

FIGURE 3. Bore-Less Centrifugal Compressor

aluminum have a strength-to-density ratio that is similar to titanium and high strength steels at the 140°F (max) operating temperature that will be experienced by the hydrogen compressor, as may be observed in Figure 4. However, unlike titanium and most steels, aluminum is recognized by the industry as being very compatible with hydrogen, not showing any susceptibility for hydrogen embrittlement.

Aluminum also helps to reduce the weight of the rotor, which leads to an improved rotor dynamic stability at the 60,000 operating speed. A rotor stability and critical speed analysis has confirmed that the overhung design is viable.

The project team includes researchers at Texas A&M (Dr. Hong Liang) who are collaborating with Concepts NREC to confirm the viability of aluminum alloys for this compressor application. A test protocol has been established based on a series of discussions with notable researchers in several national laboratories including:

1. Sandia National Laboratories (fracture mechanics testing; Dr. Chris San Marchi).
2. Savannah River National Laboratory (specimen “charging” with hydrogen plus tensile testing with H₂; Dr. Andrew Duncan).
3. Argonne National Laboratory (Dr. George Fenske).

The test protocol includes the baseline testing of titanium alloy in order to later test the viability of surface coatings that may prohibit hydrogen embrittlement and thus allow the use of titanium. The testing is in progress as of the writing of this annual report.

The maximum hydrogen compression temperature is maintained at 140°F by providing intercoolers between each of the six stages. The intercoolers have an effectiveness of 63% and cool the hydrogen to 100°F at the inlet to each stage, thus maintaining the necessary high strength-to-density ratio required for the aluminum rotor.

The complete hydrogen pipeline compressor package that integrates all of these major components is shown in Figure 5. The complete modular package, as shown, is 26 ft long x 10 ft tall x 6 ft wide (at the base) x 8 ft wide at the control panel, approximately one-half of the footprint of a piston-type, hydrogen compressor. The packaged module can be transported to the installation site as a pre-assembled package with a minimum of final alignment, water piping and electrical power connections, and instrumentation and controls start-up.

FIGURE 4. Theoretical Tip Speed for Turbomachinery with Open Impeller

FIGURE 5. Hydrogen Compressor Packaged Assembly

Conclusions and Future Directions

The preliminary engineering and design of an advanced pipeline compressor system has been completed that meets DOE's performance goals for a reliable 98% hydrogen efficiency compressor system with a footprint one-half the size of existing industrial systems and at a projected system cost of approximately 70 to 75% of DOE's target, and a maintenance cost that is less than the \$0.01/kWh. The advanced centrifugal compressor-based system can provide 240,000 kg/day hydrogen from 350 to 1,200 psig high for pipeline-grade service. This has been accomplished by utilizing a state-of-the-art aerodynamic and structural analysis of the centrifugal compressor impeller to provide high pressure ratios under acceptable material stresses. The technical approach that has been successfully implemented includes using commercially available, and thus proven,

bearings and shaft seal technology. This technical approach reduces the developmental risk and increases system reliability while maintaining a competitive cost.

The resultant design provides a compressor that not only meets DOE's Hydrogen Plan for future (but near-term) pipeline delivery, but also a compressor package that can be used by the industrial, hydrogen gas industry where there is presently 1,200 miles of pipeline providing 9 million tons per year of hydrogen gas for industrial process chemical applications. The collaborative team that has been assembled consists of an industrial user, Praxair (who has engineering experience in pipeline compressors), a materials researcher (Texas A&M), and a hydrogen refueling industry consultant (HyGen Industries) who are all committed to producing the first commercially reliable hydrogen compressor for hydrogen pipeline delivery.

Future efforts include:

Complete Current Phase 1 Effort

- Continue to update compressor station Performance and Cost Module:
 - Including reliability of individual compressor components and the maintenance costs (\$_{O&M}/kg/day) for centrifugal compressors working with hydrogen.
 - Programming a more “user-friendly” version of the Performance and Cost Model that could be used as a spreadsheet Macro to DOE's HDSAM v.2 Economics Model.
- Outline compressor start-up and shut-down strategy.
- Review present hydrogen safety standards and commercial systems and future requirements.
- Complete materials testing with Texas A&M.
- Go/No-Go decision (July, 2009).

Phase 2. Detailed Design (August 2009 to April 2010)

- Detailed subsystems modeling.
- Detailed integrated systems analysis.
- Critical components design, testing, and development.

Phase 3. System Validation Testing (May 2010 to June 2011)

- Component procurement.
- Two-stage centrifugal compressor system assembly.

Special Recognitions & Awards/Patents Issued

1. Provisional patent application filed on several innovations to centrifugal compressor design.

References

1. DOE Multi-Year Research, Development, and Demonstration Plan.
2. “Evaluation and Application of Data Sources for Assessing Operating Costs for Mechanical Drive Gas Turbines in Pipeline Service”, Dr. Anthony Smalley *et al.*, Transactions of ASME Vol. 122, July 2000.
3. “Benchmarking the Industry: Factors Affecting Compressor Station Maintenance Costs” by John Harrell, Jr., and A. Smalley of Southwest Research Institute (a presentation at the GMRC Gas Machinery Conference, Oct., 2000).

III.6 Advanced Sealing Technology for Hydrogen Compression

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Contract Number: DE-FG02-07ER84779

Project Start Date: August 15, 2008

Project End Date: August 14, 2010

TABLE 1. Technical Targets for Hydrogen Compression

Category	2005 Status	FY 2012	FY 2017
Reliability	Low	Improved	High
Energy Efficiency	98%	98%	>98%
Capital Investment (\$M) (based on 200,000 of H ₂ /day)	\$15	\$12	\$9
Maintenance (% of Total Capital Investment)	10%	7%	3%
Contamination	Varies by Design		None

Accomplishments

- Performed preliminary static tests using the seal design established in Phase I. Flow factor data (for seal leakage analysis) both in air and helium obtained for the preliminary designs of MiTi®. Seals indicated that very low leakage rates can be obtained.
- Developed a new analytical method that combines finite difference fluid mechanics analysis and finite element structural analysis as an efficient and robust method for analysis of high-speed seal designs.
- Designed and evaluated two test rigs for low-speed and high-speed dynamic testing of foil seals. Comprehensive rotor dynamic analysis of these test rigs demonstrated that the test rigs should provide smooth rotation for testing of foil seals at a wide range of speeds.

Introduction

The objective of this Small Business Innovation Research project is to develop and demonstrate the feasibility of using a close-clearance, non-contacting, and dynamic compliant foil seal in hydrogen and/or natural gas pipeline compressors. The goal of this seal is to enhance the economic viability of hydrogen as an energy carrier and to substantially improve the efficiency of centrifugal compressors so that they become feasible for use in transportation and delivery of hydrogen. Under Phase I, MiTi completed the design of a compliant foil seal suitable for the previously sized hydrogen transportation and delivery compressors and fabricated the designed seal and tested it statically to assess the leakage flow as a function of differential pressure. Results showed considerably reduced leakage with the

Objectives

Develop and demonstrate feasibility of using a close clearance, non-contacting, and dynamic compliant foil seal in hydrogen and/or natural gas pipeline compressors.

- Reduce leakage rate of hydrogen.
- Reduce system cost and increase reliability.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Delivery section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (B) Reliability and Costs of Hydrogen Compression
- (I) Hydrogen Leakage and Sensors

Technical Targets

This project is directed towards the development of oil-free gas seal technology for hydrogen transportation and delivery compressors. The developed foil seals will be tested to assess the leakage flow as a function of differential pressure. The project addresses the DOE technical targets from the Hydrogen Delivery section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan shown in Table 1.

foil seal over other technologies and previous versions of the compliant foil seal. Under Phase II, the foil seal design is to be refined based upon lessons learned from Phase I; additional static testing is to be conducted to validate the design; and finally, dynamic testing of the final full-scale design will be completed to demonstrate that performance capabilities meet the specified needs of a hydrogen transportation and delivery compressor.

Approach

Additional testing will be performed using the seal design and hardware developed under Phase I to further characterize the secondary/tertiary losses and to assess approaches to reduce the secondary losses. The design will be revised to mitigate secondary leakage losses. Full-scale compliant foil seals will be tested under dynamic rotating shaft conditions. The critical foil seal dimensions and operating clearances will be selected to minimize leakage between stages of a hydrogen transportation centrifugal compressor capable of delivering up to 1,000,000 kg/day. Ambient hydrogen gas pressures, pressure rise per stage, shaft surface speed and expected rotor motions will be included in the analysis and seal design. A new test rig (or modifications to an existing test rig) will be developed to evaluate and characterize the seals under realistic operating conditions of speed, rotor radial displacements and differential pressures. The full-scale seals will be evaluated with the dynamic test rig to determine leakage and differential pressures representative of that expected in an operating hydrogen centrifugal compressor. During testing key parameters, such as upstream and downstream pressure, leakage flow, shaft speed, rotor radial motions and seal foil, temperatures will be measured. Based upon test data, the compliant foil seal design will be revised to address identified areas for improvement. A final report documenting the key seal design parameters and component sizing, the test results and an assessment of the benefits of the seal to the performance of hydrogen compressor will be prepared.

Results

Several variations of the baseline seal configuration were evaluated under static flow conditions (i.e., no shaft rotation). Parameters investigated included number of top foils, primary bump size, radial clearance and direction of flow through the seal. During each test, the gas inlet pressure and mass flow into the seal were measured in order to determine seal leakage rate, both in total mass flow and flow factor.

Since previous testing revealed that leakage through the seal secondary passages could be reduced by modifying the seal design: preliminary testing with different seal configurations was conducted. The results of tests performed with different seal configurations

are shown in Figure 1. Modification of the seal design significantly reduced leakage by sealing the secondary flow path. While this improvement is seen in the static seal test, the effect of rotation on seal performance will be determined when the dynamic test rig becomes available for use.

A series of experiments was performed to test the effects of leakage as a function of bump height and different radial clearances. Larger bumps allow the seal to accommodate greater radial excursion by the rotor; and as expected, larger radial clearance causes larger leakages.

The back face of the static seal test chamber was modified to have a controlled orifice so that different downstream pressures could be evaluated while still achieving the same differential pressures. The modified rig for static seal testing is shown in Figure 2. High pressure bottled air and helium were used at differential pressures up to 100 and 250 psig, respectively, in these tests. To address the influence of compressibility on the gas, the tests were conducted at both ambient and elevated downstream pressures. In addition, the seal durability was assessed under continuous high differential pressures.

The three potential leakage paths were identified, where the primary flow runs in parallel with the shaft, the secondary flow travels up the front face of the flange fingers and down their back face, and the tertiary flow travels through the finger slots. The seals with two, three and four smooth foil layers were tested to increase the flow resistance in the region of the flange fingers. To characterize the losses through each leak path, the total leakage was measured first. The smooth foil surface that runs in parallel with the shaft was then “glued” to the shaft to eliminate leakage through the primary path

FIGURE 1. Static Sealing Improvement of a Radial Foil Seal

FIGURE 2. Modified Static Seal Test Rig

and, thus, allow measurement of leakage through both the secondary and tertiary paths. Next, a polymer ring replaced the face bumps to further eliminate the leakage through the secondary path; therefore, the leakage only through the tertiary path could be determined.

The flow factors for several foil seal configurations in helium are compared in Figure 3. The flow factor can be substantially decreased by modifying the foil seal design.

Two durability tests were conducted with a two-foil seal under continuous high differential pressures. The test in helium was carried out first and the seal subjected to a differential pressure of 100 psig for about seven minutes. The same seal continued to be tested in air. The seal was subjected to high differential pressure up to 100 psig for more than ten minutes. The seal was examined after these two tests and no sign of any damage was observed.

In order to properly design a high-efficiency foil seal, a universal model is needed for the analysis. This model should be readily modified to take into account various seal/hydrodynamic compliant surfaces under hydrostatic loading (differential pressure across the seal plus hydrodynamic pressure due to runner velocity and eccentricities). While present MiTi[®] analytical computer programs can be used for this task, they do not include a provision for the reaction of the top elastic and smooth foil to the applied pressure and the deformation of the underneath compliant elements. By including smooth foils and possibly surface coatings, we will have a better understanding of fluid film thickness variations in between the bearing/seal interfaces. A numerical technique has been developed to merge finite element analysis (FEA) with finite difference analysis (FDA) and has been proven to provide successful results. This technique combines the governing equations of elasticity with hydrodynamics and solves multi-level, non-linear

Comparison of Flow Factors
Baseline Design vs Design Modifications
to Reduce Secondary Leakage

61209-F001

FIGURE 3. Comparison of Flow Factor up to 100 psig for the Several Foil Seal Configurations

algorithms using the above numerical methods. We have basically taken advantage of each numerical method's strength and have combined them in such a way, enabling us to achieve numerical convergence, reduce the number of iterations needed for the computations and enhance our understanding of compliant foil seal behavior under various fluid film pressures.

One smooth top foil pad of the compliant surface foil seal was modeled as a 2-dimensional shell. The model included 51 nodes in the tangential direction and 11 nodes in the radial direction. A finer mesh was used in the trailing portion due to the higher pressures expected in that region from the hydrodynamic film calculations. The bump foils were modeled as grounded spring elements at the nodes of the shell elements. A total of 500 quadrilateral 2-dimensional shell elements and 561 point elements were used in the finite element model.

Based on the initial foil seal geometry and boundary conditions, the stiffness of the bump foils was calculated using a custom finite difference program. Applying the local pressure-deflection relationship, the pressure profile was predicted through the hydrodynamic finite difference analysis. In the finite element model, the leading edge was kept fixed in all degrees of freedom. The pressure profile predicted by the hydrodynamic analysis was applied at the nodes of the shell elements as element variable pressure. The stiffness values accounting for the bump foils from the finite difference program were converted to the spring constants at the nodes of the shell elements in order to take the variation in element sizes into account. The linear static structural analysis by finite element method was conducted using MD Nastran from MSC Software Corporation.

Using the pressure profile provided by the hydrodynamic analysis and the deformation results computed by the structural FEA, the stiffness values that include the effects of both the smooth top foil and bump foils can be calculated. These new stiffness values are then used in the next iteration of the hydrodynamic analysis. This procedure repeats until the pressure solution converges.

The seal design and analysis technique was used to perform a parametric study. In each case, three conditions were analyzed, where the first one has a uniform mesh in the angular direction with constant bump stiffness at all nodes, the second one has a finer mesh near the trailing edge in the angular direction with constant bump stiffness, and the third one has a uniform mesh in the angular direction with variable bump stiffness generated by iterations between the FDA and FEA. The un-deformed and deformed shapes of the smooth foils from the structural FEA were determined for each case. The modeling and analysis techniques developed will be used for design analysis of the desired foil seals for the hydrogen compressor.

An existing test rig was modified and refurbished for seal testing under dynamic conditions (i.e., rotating shaft). This hardware consists of a MiTi[®] 42 hp, 60,000 rpm, oil-free motor, a high-speed quill coupling and a rolling element supported spindle. The shaft of this spindle was modified to accept an existing precision test journal. The grease packed angular contact bearings in the spindle have a speed limitation of 15,000 rpm. This configuration will allow testing at up to 75% of the target surface velocity for the project. A separate, oil-free seal test spindle is being designed to allow testing up to the maximum desired surface speed.

The dynamic stability of the test rig was analyzed to ensure stable operation. The rotordynamic analysis indicated that all anticipated rotor motions would be within the system capabilities. The low-speed test rig shown in Figure 4 has been fabricated and evaluated. The test assembly was operated at speeds up to 14,000 rpm where synchronous rotor response reached a maximum of 0.002 inches peak. Shaft radial motion was monitored with eddy current proximity probes. The fast fourier transform spectrums of the experimental rotor displacements measured by two orthogonal sensors at the middle of the seal location for a similar set of speeds were compared with the predicted values.

Two separate foil seals were tested simultaneously. A total of 19 runs were performed in the low-speed test rig. Testing included static and dynamic testing with varying the differential pressure and rotational speed. The foil seals were initially tested with two top foils. In order to improve the sealing performance, a third top foil was added to provide a more tortuous path and reduce secondary leakage. Typical leakage and flow factor results are shown in Figure 5. At 14,000 rpm and

FIGURE 4. The Low-Speed Test Rig Driven with the MiTi[®] electric motor

FIGURE 5. Leakage and Flow Factor Data as a Function of Speed

75 psi pressure, a low flow factor of nearly 0.012 was achieved.

Results obtained with the 14,000 rpm test rig have successfully demonstrated stable dynamic performance of a foil seal at surface velocities very near the proposed 650 ft/sec. For these dynamic verification tests, leakage rates of the present seal design are larger than predicted because radial shaft clearance was kept larger than necessary. Now that dynamic baseline performance is demonstrated, tighter radial clearances will be tested and leakage rates will decrease drastically.

A high-speed test rig is needed to conduct dynamic testing of the seals at rotational speeds up to 60,000 rpm. Several design iterations were considered and evaluated, and the corresponding rotor dynamic analysis was conducted to predict the system stability. The final design consists of a permanent-magnet motor drive, a coupling and an interchangeable seal test journal attached to the spindle through a tie bolt. The motor is supported by two mechanical ball bearings and the spindle is on two foil journal bearings. Detailed

drawings have been prepared and the required components are being acquired to fabricate the test rig.

Conclusions and Future Directions

The tasks selected for the first year have been successfully completed. The results of static flow tests, in which various seal parameters were varied, indicated that very low leakage values could be obtained. A new analytical method that combines finite difference fluid mechanics analysis and finite element structural analysis was developed for analysis of high-speed seal designs. Several possible seal designs were evaluated with the developed analytical method. Two test rigs were designed for low-speed and high-speed dynamic testing of foil seals. Comprehensive rotor dynamic analysis of these test rigs demonstrated that the test rigs should

provide smooth rotation for testing of foil seals at a wide range of speeds. Fabrication and check out of the low-speed test rig was completed. The high-speed test rig is currently under construction. The following tasks are planned for next year:

- Finalize the design of the oil-free foil seals.
- Fabricate and fully evaluate performance of selected seals.
- Modify the seal design if necessary.
- Prepare the final report.

FY 2009 Publications/Presentations

1. "Oil-Free Rotor-Bearings and Seals for Hydrogen Compression," DOE Hydrogen Program Annual Review and Peer Evaluation Meeting, May 2009, Arlington, VA.

III.7 Development of Highly Efficient Solid-State Electrochemical Hydrogen Compressor

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Contract Number: DE-FG02-07ER84772

Subcontractor:
Sustainable Innovations, LLC, Glastonbury, CT

Start Date: June 20, 2007
End Date: August 14, 2010

Objectives

- Demonstrate feasibility of a solid-state electrochemical hydrogen compressor (EHC) cell capable of compressing hydrogen from near-atmospheric pressure to up to 6,000 psi.
- Increase the cell performance (reduce power consumption, improve compression efficiency) while lowering the cost compared to previous designs.
- Study thermal and water management to increase system reliability and life.
- Scale up EHC to a short stack.

Technical Barriers

This project addresses the following technical barrier from the Hydrogen Delivery section (3.2) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

(B) Reliability and Costs of Hydrogen Compression

Technical Targets

This project is directed at demonstrating the feasibility of solid-state electrochemical hydrogen compression. The EHC is an enabling device for low-cost hydrogen delivery. Phase II goals include the following:

- Compress hydrogen from 300 psi to up to 6,000 psi.
- Develop multi-cell stack design and validate in a short stack.
- Demonstrate compression ratio up to 300:1.
- Achieve stack performance stability at 3,000 psi for 500 hours.
- Increase hydrogen recovery efficiency to 98%.

The ultimate goal of the project is to meet the DOE targets for forecourt compressors [1].

Accomplishments

- Compression Efficiency: Reduced specific energy consumption by 70% compared to the best Phase I result (Figure 1).
- EHC Scale Up: Cell technology scaled up from single cell to 3-cell stack.
- Compression Mode Operation: Demonstrated compression ratio of 300:1 in a single step.
- Operation Hours: >6,000-hour cumulative EHC operation at different conditions.
- Hydrogen Recovery: Achieved 95% hydrogen recovery rate in the 3-cell stack.

Introduction

With the depletion of fossil fuel reserves and a global requirement for the development of a sustainable economy, hydrogen-based energy is becoming increasingly important. Production, purification and compression of hydrogen represent key technical challenges for the implementation of a hydrogen economy, especially in the transportation sector where on-board storage of pure hydrogen may be required at pressures up to 10,000 psi and compression of the hydrogen fuel up to 12,000 psi.

The level of maturity of current hydrogen compressor technology is not adequate to meet projected infrastructure demands. Existing compressors are inefficient and have many moving parts, resulting in significant component wear and therefore excessive maintenance. New technologies that achieve higher operational efficiencies, are low in cost, safe and easy to operate are therefore required. This project addresses high-pressure hydrogen needs by developing an efficient, low-cost, solid-state EHC.

Approach

The approach to address the Phase II goals consists of the following major elements:

- Build on Phase I experience to develop high-pressure stack design.
- Flow field design to increase hydrogen recovery efficiency.
- Reduce capital cost by reducing catalyst loading and simplifying system design.
- Reduce operating cost by improving membrane and electrode design.

To this end, the approach includes the construction and evaluation of advanced stack architecture, and the development and demonstration of critical sealing technology to contain the high-pressure hydrogen within the cathode compartment of the stack.

Results

The EHC cell architecture has been improved to reduce energy consumption. A 70% reduction in specific energy consumption compared to Phase I has been achieved, as shown in Figure 1. The goal of demonstrating a compression ratio of 300:1 has been met. Moreover, the EHC has been scaled up from a single cell to a 3-cell stack. It was designed, fabricated and tested for ~1,000 hours, reaching pressures up to 3,000 psi. A hydrogen recovery rate of 95% has been demonstrated in the 3-cell stack.

FIGURE 1. Significant Reduction in EHC Specific Energy Consumption Achieved

Conclusions and Future Direction

We have reduced the specific power consumption of the EHC by 70% and successfully demonstrated the feasibility of a multi-cell solid-state EHC. For the remainder of the Phase II effort, further work is suggested as follows:

- Increase pressure capability of EHC cell from 3,000 to 6,000 psi.
- Validate multi-cell stack design in a 10-cell stack.
- Further reduce power consumption to 70% of current design.
- Increase hydrogen recovery to 98%.
- Estimate capital and operating cost benefits.

Special Recognitions & Awards

This work was awarded the 2009 DOE Hydrogen Program R&D Award during the DOE Hydrogen Program Merit Review and Peer Evaluation Meeting in Washington, D.C.

FY 2009 Publications/Presentations

1. L. Lipp, "Development of Highly Efficient Solid State Electrochemical Hydrogen Compressor (EHC)", 2009 DOE Hydrogen Program Merit Review and Peer Evaluation Meeting, Washington, D.C., May 19, 2009.

References

1. HFCIT MYRDD Plan, Table 3.2.2 "Technical Targets for Hydrogen Delivery", section on Forecourt Compressors, page 3.2-14.

III.8 Hydrogen Pipeline Compressors

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Project Start Date: October 2006
Project End Date: September 2012

Objectives

- Develop advanced materials and coatings for hydrogen pipeline compressors.
- Achieve greater reliability, greater efficiency, and lower capital investment and maintenance costs in hydrogen pipeline compressors.
- Research existing and novel hydrogen compression technologies that can improve reliability, eliminate contamination, and reduce cost.

Technical Barriers

The project addresses the following technical barrier from the Hydrogen Delivery section (3.2.4.2) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

(B) Reliability and Costs of Hydrogen Compression

Technical Targets

This project is directed toward the study of fundamental mechanisms associated with the tribology of hydrogen pipeline compressors (friction, wear, and degradation). The goal of the research is to identify materials and engineered surface treatments that provide low friction and wear resistance required to achieve the energy efficiency and reliability targets for pipeline compressors. Accordingly, the project tasks address the challenges associated with meeting the DOE hydrogen delivery performance and cost targets for 2012:

Technical Targets for Hydrogen Delivery

Category	FY 2012 Targets	2009 Status
Reliability	Improved	Low
Energy Efficiency	98%	<98%
Total Capital Investment	\$12M	>\$15M
Maintenance	7%	>10%
Contamination	Varies	Unknown

Accomplishments

- Bid requests for a high-speed high-temperature tribometer were sent out, and a satisfactory bid was received.
- Construction of the tribometer was started in February 2009, and delivery to Argonne is scheduled for August 2009.
- The ability to run tests in an environment of pure methane (simulating natural gas) was added.
- Room-temperature tests in pure hydrogen and methane were run to compare the friction and wear behavior of baseline materials and coated materials/ novel composites and conversion coatings.

Introduction

Compressors are critical components used in the production and delivery of hydrogen. Current reciprocating compressors used for pipeline delivery of hydrogen are costly, are subject to excessive wear, have poor reliability, and often require the use of lubricants that can contaminate the hydrogen (used in fuel cells). Duplicate compressors may be required to assure availability.

The primary objective of this project is to identify, and develop as required, advanced materials and coatings that can achieve the friction, wear, and reliability requirements for dynamically loaded components (seal and bearings) in high-temperature, high-pressure hydrogen environments prototypical of pipeline and forecourt compressor systems.

The DOE Strategic Directions for Hydrogen Delivery Workshop identified critical needs in the development of advanced hydrogen compressors – notably, the need to minimize moving parts and to address wear through new designs (centrifugal, linear, guided rotor, and electrochemical) and improved compressor materials. The DOE is supporting several

compressor design studies on hydrogen pipeline compression specifically addressing oil-free designs that demonstrate compression in the 0–500 psig to 800–1,200 psig range with significant improvements in efficiency, contamination, and reliability/durability.

One of the designs by Mohawk Innovative Technologies Inc. (MiTi[®]) involves using oil-free foil bearings and seals in a centrifugal compressor, and MiTi[®] identified the development of bearings, seals, and oil-free tribological coatings as crucial to the successful development of an advanced compressor [1]. MiTi[®] and ANL have developed potential coatings for these rigorous applications; however, the performance of these coatings (as well as the nickel-alloy substrates) in high-temperature, high-speed hydrogen environments is unknown at this point.

Approach

Our approach is to evaluate the tribological performance of seals and bearing materials under consideration by MiTi[®] and provide them with the data required to select the optimum seal and bearing material/coating configuration for the 300-kg/min centrifugal compressor that was designed in their Phase II studies. This effort includes: a) evaluating the effects of the hydrogen environment on the mechanical properties of Ni alloys; b) determining the feasibility of coating-suitable substrates with Argonne, MiTi[®], and outside vendor coatings, [2]; c) establishing the requirements and testing needs for implementing near frictionless carbon (NFC) and MiTi[®]'s series of foil seal coatings; and d) testing foil seal and bearings under conditions prototypic of their proposed hydrogen compressor.

The research uses facilities and expertise at Argonne – notably the ability to deposit advanced high-performance coatings (NFC), to test and evaluate coatings under extreme conditions, and to characterize and understand friction, wear, and surface degradation phenomena that determine component lifetime and reliability.

Different contact stress/sliding speed regimes were identified, depending on compressor design:

- Positive displacement compressors - high contact stress, low sliding speed.
- Axial flow compressors - high speed, low contact stresses.
- Centrifugal compressors - intermediate speeds and contact stresses.

Based on the range of contact stresses and sliding speeds anticipated for these compressors, we will replicate lab conditions to encompass nominal contact stresses between 2 and 1,500 psi, with sliding speeds

from 0.1 to 10 m/s. Operating temperatures up to 500°C due to working-gas adiabatic heating and flash/asperity heating can add an additional 500 to 750°C (depending on load, speed, thermal properties, and friction) to the temperature of near-surface asperities. Coating deposition on substrates focuses on NFC and commercial coatings based on conventional solid lubricants. The substrates chosen are stainless steel, nickel alloys, and Cr-Mo steels.

The effect of gas composition has not been defined. Different levels of impurities (moisture, natural gas, contaminants) will affect formation of surface films. Lab tests will be performed with H₂ containing different levels of water and other trace impurities and will use natural gas to establish the baseline performance of current compressors.

Results

During Fiscal Year 2009, a new data acquisition system was installed on the room-temperature tribometer that is being used for ongoing tests of candidate materials for compressors. Various conditions were used to compare sliding in hydrogen vs. methane, determine friction of new thin film coatings, and evaluate a chemical conversion process. Figure 1 shows the upgraded hydrogen/methane tribometer and subsystems.

A large amount of sliding data was obtained in FY 2009. The baseline materials studied included a Hastelloy X and Type 316 stainless steel (316ss). Zirconium is reported to form hydrides that have beneficial frictional properties, but no improvement due to sliding in hydrogen was observed. A new carbon fiber material was tested. The hydrogen effect on the carbon was not beneficial as first anticipated.

The high-temperature tolerance of a very promising coating (Argonne's NFC6) was tested and found to be quite good. In addition, a new coating, MoS₂/graphite, was tested, as was a conversion coating, pack boriding.

FIGURE 1. Photograph of Room-Temperature Tribometer and Subsystems

Figure 2 shows friction coefficient results for the MoS_2 /graphite and NFC6. The tribological behavior for long duration (one hour) sliding in hydrogen gas of a commercial MoS_2 /graphite coating is shown in Figure 2a. For this test the thrust washer speed was ramped to 2,000 rpm and back down every 100 s. The friction coefficient remained fairly high at 0.4. The friction coefficient as a function of test temperature for Argonne's NFC6 tested against itself in an inert environment (N_2) is shown in Figure 2b for a pin-on-disk test configuration at slow speed. The friction at room temperature retains a low and desirable value with increasing temperature. However, upon reaching 350°C, the friction coefficient increases suddenly by about a factor of 60, indicating catastrophic change in the surface chemistry. A repeat test on the same sample (second trace), but different wear track/region, still showed acceptable performance, although these results raise concern about a potential thermal annealing effect on tribological performance.

The fabrication method for the new conversion coating, pack boriding, uses a commercially available salt bath to chemically transform the surface without the need for a coating step. Tests showed high friction

FIGURE 2. Friction coefficients of (a) one-hour thrust-washer test of commercial MoS_2 /graphite coating sliding against bare Hastelloy X750 nickel surface in air and (b) NFC6/NFC6 sliding at elevated temperatures in N_2 (pin-on-disk configuration).

in both air and hydrogen, with erratic coefficients of friction.

Most of the tested materials were examined by analytical techniques such as optical microscopy and optical profilometry. In the future, the near-surface properties will be examined by nanoindentation. Optical examination of most materials showed clear evidence of material adhesion and transfer as a mechanism by which wear proceeds.

Some of the materials behaved differently, depending on whether they were tested in methane or hydrogen. Although the coefficients of friction are comparable, the Argonne N3FC material tested in methane (Figure 3 – top) produced a much weaker transfer film on the counterface surface than when tested in hydrogen (Figure 3 – bottom). This finding may have implications for incorporating existing natural gas compressor technology (methane) into hydrogen gas compressors.

The diamondlike carbon (DLC) films that were available in FY 2009 were conventionally produced plasma-grown NFC from Argonne, and a second type of DLC called “N3FC,” which was produced from a solid carbon target. It was believed that N3FC has properties superior to NFC because of some low-speed sliding tests that were done. These tests found that the low friction

FIGURE 3. Optical micrograph of transfer films on surface slid against Argonne N3FC in pure methane (top) and pure hydrogen (bottom) showing weaker transfer film for methane.

was attained much quicker for the N3FC. However, for the high-speed and low-pressure tests performed in conditions prototypic of compressor use, the conventional NFC shows low friction and withstands high loads without any obvious distress. In contrast, N3FC displays higher friction and undergoes apparent damage after the load test.

Table 1 summarizes the friction coefficients of several materials studied in this project. The table has been updated with the most recent result, focusing on results in either pure methane or pure hydrogen. MoS₂/graphite is a commercial bonded material; CF comp is a carbon-fiber composite, and N3FC is a Argonne-developed thin hard carbon coating that is produced by sputter deposition. NFC6 is an Argonne-developed thin hard carbon coating that is produced using plasma-enhanced chemical vapor deposition.

A number of coatings have been indentified as promising candidates, and each has features attractive for high-speed hydrogen-environment use, but needs to be proven by testing. The coatings fall in the following areas:

- Carbon-carbon composite.
- Composites such as Korolon, Molykote MoS₂/graphite.
- Intermetallics such as Tribaloy or tungsten carbide + 17%Co.

- Compounds such as boron nitride composite, boride fused, MoS₂ or Bodycote.
- Carbon-based compounds such as ANL DLC6, ANL N3FC, Ionbond, Diamonex, and K-Systems DLC.

Conclusions and Future Directions

Progress was made on establishing the tribological properties of baseline materials and coatings in FY 2009, though hampered by the lack of high-speed high-temperature testing capability. A total of 81 separate tests were performed, and baseline materials produced unacceptably high friction and wear, whereas a carbon-based coating, NFC6, looked most favorable.

Bid requests for a high-speed high-temperature tribometer were sent out, and a satisfactory bid was received. Construction of the new tribometer was started in February 2009, and delivery is scheduled for August 2009. Installation of the new test machine will enable tribological testing under conditions more representative of those experienced in actual bearing/seal service.

FY 2009 Publications/Presentations

1. Impact of Friction Reduction Technologies on Fuel Economy, G. R. Fenske, presented to Chicago Section STLE, March 2009.

TABLE 1. Friction Coefficients of Materials in Different Environments

Rotating Face	Stationary Counterface	Environment	Friction	Wear Face	Wear Counterface
MoS ₂ /graphite	X750	Air	Medium 0.4	High - abrasion	Low
MoS ₂ /graphite	X750	Hydrogen	Medium 0.4	High - abrasion	Low
Zr	Zr	Air	Medium 0.5	High - galling	High - galling
Zr	Zr	Hydrogen	Medium 0.5	High - galling	High - galling
Boride	316ss	Air	Med high 0.6	Low - abrasion	Low
Boride	316ss	Hydrogen	Med high 0.6	Low - abrasion	Low
CF comp	X750	Air	Medium 0.4	Low	Low
CF comp	X750	Hydrogen	Medium 0.4	Low	Low
CF comp	X750	Methane	Medium 0.4	Low	Low
N3FC	4118 steel	Hydrogen	Low 0.15	Low	None
N3FC	4118 steel	Methane	Low 0.15	Low	None
HX	Hastelloy X	Hydrogen	Very high > 1	High - galling	High - galling
HX	Hastelloy X	Methane	Very high > 1	High - galling	High - galling
NFC6	316ss	Air	Low (0.2-0.4)	Low	None
NFC6	316ss	Hydrogen	Very Low (0.04)	Low	None
X-750	X-750	Hydrogen	High 0.6-0.9	High	High
316ss	316ss	Hydrogen	High 0.6-0.9	High	High

2. Hydrogen Pipeline Compressors, George Fenske (Primary Contact) and Robert Erck, in 2008 Progress Report for the DOE Hydrogen Program.
3. Friction and Wear Properties of Materials Used in Hydrogen Service, R.A. Erck, G.R. Fenske, and O.L. Eryilmaz, presented at Materials Innovations in an Emerging Hydrogen Economy Conference, February 24–27, 2008, Cocoa Beach, FL.
4. Friction and Wear of Metals and Coatings Used in Hydrogen Service, R.A. Erck, G.R. Fenske, and O.L. Eryilmaz, presented at 2008 International Hydrogen Conference Effects of Hydrogen on Materials, September 7–10, 2008, Jackson, WY.

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1. H. Heshmat, P. Hryniewicz, J.F. Walton II, J.P. Willis, S. Jahanmir, and C. DellaCorte, *Tribol. Intl.* **38**, 1059–1075 (2005).
2. A. Erdemir, O.L. Eryilmaz, and G. Fenske, *J. Vac. Sci. Technol. A* **18**(4), 1987–1992 (2000).

III.9 Advanced Hydrogen Liquefaction Process

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Contract Number: DE-FG36-08GO18063

Project Start Date: June 1, 2008

Project End Date: May 31, 2011

Objectives

Develop a low-cost hydrogen liquefaction system for 30 and 300 tons/day:

- Improve liquefaction energy efficiency.
- Reduce liquefier capital cost.
- Integrate improved process equipment invented since last liquefier was designed.
- Continue ortho-para conversion process development.
- Integrate improved ortho-para conversion process.
- Develop optimized new liquefaction process based on new equipment and new ortho-para conversion process.

Technical Barriers

This project addresses the following technical barrier from the Production section (3.2.4) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (C) High Cost and Low Energy Efficiency of Hydrogen Liquefaction

Technical Targets

TABLE 1. Technical Targets for Liquid Hydrogen Delivery

Characteristic	Units	2012 Target	2017 Target
Small Scale Liquefaction (30,000 kg/day)			
Installed Capital Cost	\$	40M	30M
Energy Efficiency	%	75	85
Large Scale Liquefaction (300,000 kg/day)			
Installed Capital Cost	\$	130M	100M
Energy Efficiency	%	>80	87

We are addressing the capital cost and energy efficiency targets. We are not at the point in the project where we know enough about possible energy savings or capital cost reduction to show quantitative progress toward the goals yet.

- Capital Cost:
 - Improved process design.
 - Improved process equipment.
- Energy Efficiency:
 - Increased equipment efficiency.
 - Improved process efficiency.
 - Improved ortho-para conversion efficiency with a goal of reducing energy required for ortho-para conversion by at least 33%.

Accomplishments

- Constructed improved test unit capable of operating over a temperature range from 77 K to about 150 K.
- Developed spreadsheet model to calculate energy requirements for hydrogen liquefaction.
- Identified problems with commercial process simulation software for modeling ortho and para hydrogen and worked with program supplier to develop a plan for solving the problems.
- Prepared and tested new materials for improved ortho-para conversion using recipes and equipment that produce materials similar to those that could be produced in commercial quantities.

Introduction

Hydrogen liquefiers are highly capital intensive and have a high operating cost because they consume a significant amount of electrical power for refrigeration. There are only a few hydrogen liquefiers in the world and only six currently operating in the U.S. These plants are not built frequently, so they have not been thoroughly optimized for today's equipment. Furthermore, many of them were built when power was much less expensive than it is today, so those plants do not have optimized efficiency.

Approach

This project focuses on improving liquefier efficiency and reducing overall liquefaction cost, including reducing capital cost. The project will attempt to accomplish these goals using three different aspects of an integrated approach:

- Improved process design – Develop a more efficient refrigeration process including ortho-para conversion and refrigeration using available streams and equipment.
- Improved process equipment – Integrate improvements made in process equipment since the most recent liquefier design to take full advantage of the increased capabilities and improved efficiency.
- Improved ortho-para conversion process – Ortho-para conversion consumes a significant amount of refrigeration energy because it requires cooling at low temperatures. Improvements in ortho-para conversion can lead to a significant reduction in power requirements.

This project builds on previous work done at Praxair, some of which was part of a project funded through Edison Materials TEchnology Center (EMTEC). The previous project demonstrated that the improvements in ortho-para conversion were possible, but developing the complete optimized process design was beyond the scope of the project.

Results

The material screening test system used during the EMTEC project has been recommissioned to perform additional material testing. We are developing new materials to test. This system can test materials at the boiling point of the cooling fluid, such as liquid nitrogen. The system can test ortho-para conversion at pressures up to 400 psig. This was a significant limitation in earlier testing because it does not allow for testing over a temperature range. It has the advantage of being a

simple system that is excellent for preliminary screening of materials. Figure 1 shows this system. New materials work has proceeded from the EMTEC project with new recipes and methods developed to provide samples with properties that more closely approximate those that would be obtained using commercial-scale materials manufacturing.

A pilot-scale system to conduct process testing on desired materials over a range of temperatures has now been built (Figure 2). All components of the system have been tested to ensure proper operation. Testing is scheduled to begin in the third quarter of 2009.

This test system is fully automated to allow for both remote control and eventual material life testing. The system consists primarily of a series of pressure vessels, each of which houses a material bed. The annular space between the inside of the pressure vessel and the outside of the material bed contains a liquid coolant that can be pressurized. The ortho-para conversion

FIGURE 1. Material Screening Test System

FIGURE 2. Pilot-Scale Test System

process is conducted at very low temperatures (<150 K) and therefore a liquid coolant such as liquid nitrogen or liquid argon is required to achieve temperatures in this range. Each pressure vessel contains a vent line equipped with a back pressure control valve to allow for control of the liquid boiling pressure. By controlling the liquid boiling pressure, temperature can be controlled indirectly over a range of 77 K to 126 K using liquid nitrogen as the coolant and temperatures up to about 150 K using liquid argon.

Modeling

Two models of existing hydrogen liquefiers have been constructed using process modeling software. The models are based on Praxair's 20 ton/day liquefiers in McIntosh, AL and Ontario, CA. The current models will utilize the Peng-Robinson Stryjek-Vera equation of state until the more accurate Modified Benedict Webb Rubin (MBWR) equation of state can be implemented into the process modeling software. The purpose of modeling the existing liquefiers is to enable the identification of possible energy savings. Thermodynamic analysis of the current process can be performed to pinpoint areas of inefficiency and lead to process design improvements.

The standard hydrogen liquefier is usually integrated with a nitrogen liquefier so that liquid nitrogen can be used in the initial cooling stage to cool the hydrogen stream down to about 75-90 K. The hydrogen stream is then split into a small and large stream. The small stream ultimately becomes the liquefied product while the large stream is sent through a series of turbine expanders and used as the refrigerant in the liquefier. The refrigerant stream is then recompressed and recycled to the beginning of the process. Compression is the most energy intensive part of the liquefaction process. Both the compression and expansion steps are areas where efficiency improvements could have a large effect on the overall energy usage of the process. Other technologies such as magnetic cooling and using helium as the refrigerant will be looked at for potential efficiency improvements.

Perhaps the largest improvement will come from the implementation of the improved ortho-para conversion process. In the current system, the heat exchangers are responsible for removing all the additional heat released during the transformation from ortho to para hydrogen. This additional heat removal results in additional power needed for the cooling loop. The improved ortho-para conversion process could significantly reduce the overall energy consumed. In order to properly model the ortho-para transformation, it is necessary to implement an accurate thermodynamics package for both ortho and para hydrogen. We are currently working with the process simulator supplier to improve the ability to model the behavior of normal and para-hydrogen.

Once the MBWR fix is completed, we will model the ortho-para conversion process and integrate it into the process model. We will also include any additional efficiency improvements into the model. We will then compare power consumption and capital cost to the current base case systems. We will include multiple energy saving solutions along with the improved ortho-para conversion process to maximize cost reduction and energy efficiency to meet the DOE goals.

While working on implementing the MBWR equations, we have also constructed a simple Excel-based model to track the energy requirements for liquefying hydrogen as a function of temperature in the cold box heat exchanger. This model gets its thermodynamic information using data supplied by the National Institute for Standards and Technology for ortho-para hydrogen. This model shows that the energy needs to be removed at a higher rate during the last 50 K or so of liquefaction. This also shows that implementing the improved ortho-para conversion process could potentially reduce the energy required for hydrogen liquefaction.

Conclusions and Future Directions

- We are working with the process simulation software vendor to fix problems modeling ortho and para hydrogen and intend to have the problem solved later this year. We will use the corrected version of the software to model different liquefaction processes to identify possible energy savings.
- Testing will begin next quarter using the new test reactor that is capable of testing ortho-para conversion over a temperature range.

FY 2009 Publications/Presentations

1. DOE Annual Hydrogen Review Meeting

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III.10 Active Magnetic Regenerative Liquefier

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Contract Number: DE-FG36-08GO18064.A000

Project Start Date: June 1, 2008

Projected End Date: December 31, 2011

Objectives

This project has several well-defined objectives selected to experimentally prove highly efficient hydrogen liquefiers. The objectives include:

- To collect/create a validated engineering basis for an advanced H₂ liquefier technology that meets or exceeds DOE's targets for both capital and energy efficiency.
 - Identify areas where more applied research is needed.
 - Examples – fabrication techniques for high performance regenerators; different configurations of superconducting magnets; and others.
- To apply our technical knowledge of and experience with active magnetic regenerative liquefaction to sequentially analyze, design, fabricate, and test experimental liquefier prototypes to validate performance simulation model used to design active magnetic regenerative liquefiers (AMRLs).
 - Especially applicable to liquefied hydrogen (LH₂), but also to other cryogenics.
- From July 2008 through May 2009, our aim has been:

- To collect AMRL design literature and create the design basis for the first lab-scale AMRL prototype; and
- To analyze, design, fabricate, and test an AMRL prototype operating from ~290 K to ~120 K with a figure of merit (FOM) >0.5.

Technical Barriers

This project addresses the following technical barriers from the Delivery section of the Hydrogen, Fuel Cells and Infrastructure Technologies Multi-Year Research, Development and Demonstration Plan:

(C) High Cost and Low Energy Efficiency of Hydrogen Liquefaction

Technical Targets

This project is developing advanced liquefier technology that offers simultaneously lower capital costs and higher thermodynamic efficiency than existing technology. Insights gained from experimental prototypes will be applied toward the design and deployment of hydrogen liquefier facilities that meet the following DOE 2010 hydrogen production and delivery targets:

- Delivery cost of <\$1.00/gge;
- \$40 MM capital cost for a liquefier with a capacity of 30 tonnes per day (TPD); and
- Operational efficiency of liquefier as defined by DOE of 75%.

Accomplishments

- Created a detailed design basis for 290 K to 120 K lab-scale AMRL prototype including:
 - Solenoidal superconducting magnet subsystem:
 - NbTi multifilament wire; potted;
 - 4 K operation; persistent mode switch.
 - Conduction cooling to 4 K via Gifford McMahon cryocooler; diode quench protection.
 - Low thermal conduction/high electrical conduction leads.
 - Reciprocating drive of dual magnetic regenerators subsystem.
 - Magnetic regenerator subsystem:
 - Rare earth alloys for refrigerants; layered materials per model.
 - Matched regenerator design; aspect ratio 1-2; 10,000 m²/m³.

- Low pressure drop; low longitudinal thermal conductivity.
- Regenerator heat transfer fluid subsystem:
 - Pressurized He gas; closed-loop circulator with reversing switch for reciprocating flow; bypass flow controls.
 - Anchored at 290 K at input to hot end of regenerators.
- External process stream:
 - Anchored at 290 K at heat sink; controllable flow.
- Cold box and structural subsystem:
 - Double walled dewar; G-10 structural braces; high vacuum experimental space.
- Instrumentation and control subsystem:
 - LabVIEW-based data acquisition system (DAS) and control.
 - Full set of temperature, pressure, mass flow, work rate, thermal loads, magnetic field sensor.
- Used the following principles to conceptually design an initial AMRL lab prototype with high FOM:
 - Use an inherently efficient thermodynamic cycle, i.e., the AMR cycle.
 - Use an efficient work input mechanism for magnetic forces.
 - Use an efficient work recovery mechanism, i.e. balanced dual regenerators.
 - Ensure small temperature approaches for all heat transfer between heat transfer and process streams by use of multiple stages.
 - Chose small dimensions of magnetic refrigerants in regenerative heat exchanger geometries to achieve high specific area.
 - Keep pressure drops for heat transfer fluid flow low with many parallel flow channels.
 - Ensure low longitudinal thermal conduction mechanisms by proper material and geometry choices.
 - Minimize frictional and parasitic heat leak mechanisms.
 - For hydrogen, perform ortho-to-para conversion at the highest possible temperature during cooling in process heat exchangers.
- Used well-defined irreversible entropy mechanisms of heat transfer, pressure drop, and longitudinal thermal conduction for high performance passive regenerators to design our active regenerators:
 - New results from AMRL performance simulation modeling show two additional intrinsic irreversible entropy mechanisms must be included:
 - Thermal mass differences during AMRL cycle due to the temperature and magnetic field dependence of the magnetic refrigerants.
 - Unbalanced heat transfer fluid flow requires bypass flow return.
- Two additional key objectives of 290 K to 120 K prototype tests are:
 - To characterize the performance of an AMRL as a function of thermal mass imbalance; and
 - To characterize the amount of bypass of the heat transfer fluid.
- The status of 290 K to 120 K AMRL lab-scale prototype is:
 - Detailed design and fabrication of magnetic regenerators are preceding well; magnetic materials are selected and raw materials ordered.
 - Superconducting magnet subsystem design is progressing well; the magnet, high temperature superconductor (HTSC) leads, persistent mode switch, diode protection, power supply and sensors are ordered.
 - Conduction cooling subsystem including cold box and Gifford McMahon cryo-cooler are already in our laboratory facilities.
 - High vacuum pump and related equipment in place for AMRL operational space.
 - Structural support members integrated with shield cooling analysis and design is substantially completed.
 - Both the heat transfer fluid and process fluid flow subsystems are in design.
 - Drive subsystem is in design.
 - The piping and instrumentation diagram is being created as the instrumentation and controls choices are made.
 - The LabVIEW DAS in our lab is being upgraded for high speed measurements.

Introduction

The primary objective of this project is to provide a validated engineering basis for the AMRL technology by analyzing, designing, fabricating, testing, and validating up to three experimental hydrogen liquefier prototypes. Prometheus Energy has extensive technical experience and unique knowledge of magnetic refrigeration technology that it is using to execute this project.

Successful demonstration of this promising technology will provide a strong incentive for integration of this type of liquefier into various hydrogen infrastructure projects such as creating thermal capacitance for hydrogen produced by electrolysis at intermittent renewable or off-peak electricity plants. It could also be easily scaled to a vehicular refueling station size where the hydrogen is produced via steam methane reformation and supplied as LH_2 and/or compressed hydrogen produced from liquid hydrogen.

Approach

We plan to model, design, build, test, and validate fully instrumented systems. The first prototype under development during the first year of this project is a single-stage active magnetic regenerative liquefier spanning from ~ 290 K to ~ 120 K.

Results

We have done extensive performance modeling with a proprietary numerical simulation code for an AMRL. An example of results of these calculations is illustrated in Figure 1. These results with a 6.4 tesla (T) magnetic field change and a heat rejection temperature of 290 K show the temperature span of a particular AMRL with two layers of magnetic refrigerants. The upper (hottest) refrigerant in the regenerator is Gd metal and the second is a homogeneous alloy of Gd with Dy whose Curie temperature was varied by choice of composition. These results show that the temperature span peaks when the Curie temperature of the second magnetic refrigerant is ~ 250 K. The relative efficiency is also illustrated in Figure 1; it also shows a broad maximum in efficiency near the same Curie temperature. Similar modeling for the AMRL predicts that with reasonable design choices it is possible to achieve relative thermodynamic efficiency for the first stage AMRL of ~ 70 -80% of ideal. This is an important requirement for achieving the high FOM of a hydrogen liquefier.

In addition to modeling the effects of layering of magnetic refrigerants in the magnetic regenerators, the effects of bypass flow of the heat transfer fluid on the performance of the magnetic

liquefier stage has been predicted. These analyses are summarized in Figure 2 that illustrates the concept and the substantial predicted improvements in performance due to bypass flow. This is the expected result because the bypass flow is returned to the hot end of the regenerator in counterflow with the process stream. The resultant reduction in temperature approach in the cold heat exchanger significantly reduces the irreversible entropy produced by cooling the process stream. This design feature is unique to AMRLs and is a very important means to improve the FOM of a hydrogen liquefier.

FIGURE 1. Calculation of the Influence of Curie Temperature on Performance of an AMRL Regenerator with $T_{\text{hot}} = 290$ K and $\Delta B_a = 6.4$ T

FIGURE 2. Calculation of Influence of Bypass Flow of Heat Transfer Fluid on AMRL Performance

FIGURE 3. Schematic Diagram of the 290 K to 120 K AMRL Lab-Scale Prototype

The mechanical design of the 290 K to 120 K lab prototype is being done based on the performance predictions from the numerical AMRL simulation code. The initial design of the prototype based on the design basis completed after the numerical modeling was completed. Figure 3 schematically illustrates a cross-section of the AMRL prototype with the arrangement of the various components of the AMRL. These include the superconducting magnet, the Gifford McMahon cycle cryocooler for conduction cooling of the magnet and thermal shield, the dual magnetic regenerators, the heat transfer fluid circulator, the process stream, the drive, the support structure, and the double-walled dewar that serves as the cold box. The actual cold box (dewar) and the two-stage Gifford McMahon cryocooler cold head in our lab are shown in Figure 4. This prototype will be an excellent test device to understand the new features of the design of a magnetic regenerator with both layering and bypass.

Conclusions and Future Directions

Heracles/Prometheus is developing the first AMRL prototype spanning this large temperature span in the world. The first lab-scale prototype is being designed to operate between ~290 K and ~120 K. It will

FIGURE 4. The AMRL cold box on the left is a double-walled Dewar. The cryocooler on the right is a proven two-stage Gifford McMahon model used for conduction cooling of the magnet and thermal shield.

experimentally answer key questions regarding the best design for layers of magnetic materials in regenerators with varying amounts of bypass flow of the heat transfer fluid. It will allow measurement of the temperature span and thermodynamic efficiency (FOM) as a function of operating parameters such as frequency, heat transfer fluid flow rate, applied magnetic field change, hot temperature, percentage of bypass flow, layering technique, and other performance measures. The experimental results will be analyzed and compared to performance simulations to further validate the numerical performance model.

Future directions of this project include using the results of the first AMRL prototype tests and validated model to design the lab-scale prototype of a multi-stage AMRL to make ~10-15 kg/day of LH_2 . The prototype spanning from ~290 K to ~20 K will be tested. It will be the first AMRL to make liquid hydrogen. We anticipate this prototype will be in testing and analysis before September 30, 2010. These results will be used to establish an engineering database for larger AMRL designs. The report obligations for this project will be completed as they become due.

III.11 Innovative Hydrogen Liquefaction Cycle

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Contract Number: DE-FG36-05GO15021

Subcontractors:

- R&D Dynamics, Bloomfield, CT
- Massachusetts Institute of Technology (MIT), Cambridge, MA

Start Date: August 1, 2005

Estimated Project End Date: August 1, 2011

Introduction

The purpose of this project is to produce a pilot-scale liquefaction plant that demonstrates Gas Equipment Engineering Corp's ability to meet or exceed the efficiency targets set by the Department of Energy. This plant will be used as a model to commercialize this technology for use in the distribution infrastructure of hydrogen fuel. It could also be applied to markets distributing hydrogen for industrial gas applications. Extensive modeling of plant performance will be used in the early part of the project to identify the liquefaction cycle architecture that optimizes the twin goals of increased efficiency and reduced cost. The major challenge of the project is to optimize/balance the performance (efficiency) of the plant against the cost of the plant so that the fully amortized cost of liquefying hydrogen meets the aggressive goals set by DOE.

This project will design and build a small-scale pilot plant (several hundred kg/day) that will be both a hardware demonstration and a model for scaling to larger plant sizes (>50,000 kg/day). Though an effort will be made to use commercial or near-commercial components, key components that will need development for either the pilot- or full-scale plant will be identified. Prior to starting pilot plant fabrication, these components will be demonstrated at the appropriate scale to demonstrate sufficient performance for use in the pilot plant and the potential to achieve the performance used in modeling the full-scale plant.

Background

The simplest liquefaction process is the Joule-Thomson expansion cycle. The gas to be liquefied is compressed, cooled in an after-cooler, and then undergoes isenthalpic expansion across a throttle valve. If the gas is cooled below its inversion temperature in a heat exchanger, then this expansion results in further cooling – and may result in liquid formation at the valve outlet. For hydrogen, this temperature is -95°F. It is obvious that this cycle alone cannot be used for liquefaction of hydrogen without any pre-cooling of hydrogen below its inversion temperature. A modification of this cycle is sometimes used in which liquid nitrogen is used to cool the gaseous hydrogen below its inversion temperature and then Joule-Thomson expansion is used to liquefy hydrogen.

Joule-Thomson expansion is inherently inefficient as there is no work done during expansion. The industrial gas industry departed from using Joule-Thomson as a

Objectives

Reduce the cost and improve the energy efficiency of hydrogen liquefaction.

- Develop and model a large capacity (50,000 kg/day or greater) hydrogen liquefaction cycle that:
 - Attain efficiencies which are a 33% improvement over present state-of-the-art systems.
 - Significantly reduce the capital expense relative to similar capacity systems.
- Identify and develop the key components needed for the H₂ Liquefaction Cycle that are not commercially available.
- Produce a small-scale (~500 kg/day) hardware demonstration of a hydrogen liquefaction plant to cost effectively demonstrate the large capacity system design and architecture.

Technical Barriers

This project addresses the following technical barriers from the Delivery section (3.2) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (C) High Cost and Low Energy Efficiency of Hydrogen Liquefaction

primary process used in liquefaction of atmospheric gases in the 1960s. Turbo-expanders or expansion engines are now used at most industrial gas plants to provide the necessary refrigeration for liquefaction. The expansion across a turbo-expander is ideally isentropic, or in other words, some useful work is done in expansion. An example of this cycle, now used in most hydrogen liquefaction plants is shown in Figure 1.

We originally proposed to use an optimized combination of the Reverse-Brayton expansion cycle (or a modified Claude cycle) with the Joule-Thompson expansion cycle. At the beginning of the project the scope was expanded to look at a broader range of alternate cycles. The original consultant (AMCS) was dropped, partially because they would not agree to the normal terms and conditions found in DOE-sponsored project contracts and partially because of the nearly year-long hiatus in the project funding. Subsequently they were replaced with MIT. We are working with the Cryogenics Laboratory there, which was originally started by Dr. Samuel Collins and now run by Dr. Joe Smith, with the assistance of Dr. John Brisson. Dr. Brisson collaborated with Mr. Shimko at GEECO and Dr. Smith to select the various cycles that were evaluated. A large portion of the modeling and evaluation, and specifically the investigation of prior work on alternate cycles and modeling was performed by Wayne Staats, a masters degree candidate. This innovative approach to the basic cycle was chosen to be pursued in the “year one” work. The resulting cycle is shown in Figure 2. It is a once-through cycle that uses a helium-based refrigeration cycle employing Reverse-Brayton turbo-machinery. The heat removal from the hydrogen stream is performed by standard two and three channel heat exchangers. The baseline modeling assumes that the catalytic heat exchangers are isothermal, though additional modeling showed the added efficiency gain by using continuous catalytic heat exchangers throughout the cycle. This became the focus of “year-two” component demonstration work.

FIGURE 1. Claude Cycle Used for Hydrogen Liquefaction

Accomplishment Summary During the Previous Year (4/1/08 to 3/31/09)

The “second year” work of the project was started this year. Due to limitations in available funding the work was limited to demonstrating the catalytic heat exchanger component determined to be critical to achieving the performance projected for the liquefier cycle design completed in “year-one”.

The results of the first year work showed that the unique liquefier cycle design results in both significantly increased efficiency (30% better) and significantly lower capital cost. In the year-two work a numerical model was developed for the catalytic heat exchanger and validated against previous testing performed on simplified catalytic heat exchangers. Based on simulations run using this model it was found that several configurations of “practical, buildable” heat exchangers can be loaded with catalytic material and effectively used in the liquefaction cycle developed in year-one. Work began on the test apparatus to test scaled-down versions of these heat exchangers. The test apparatus design was completed, para-ortho measurement devices were built and successfully tested, catalytic material acquired, compressors run the helium and hydrogen flow loops identified and tested. Work has begun on building the test apparatus.

Project Results

The following is a summary of the major work efforts and accomplishments in this reporting period. More detailed description of the project results follows.

- Completed development and validated accuracy of CHEX numerical model.

FIGURE 2. Basic Cycle Definition

- Finished design of CHEX article test apparatus.
- Model shows that typical heat exchanger channel dimensions are satisfactory for pressure drop, heat exchange, and catalyst reaction rate criteria.
- Sensor for measuring para/ortho make-up fabricated and performance verified.

The continuous catalyst numeric model was assembled and successfully tested against known data. The model uses MATLAB for controlling inputs, outputs, and referencing thermophysical properties, and COMSOL Multiphysics for the finite element computations.

The model breaks the heat exchanger into alternating lengths of adiabatic conversion and “normal” heat exchange. Figure 3 shows this arrangement pictorially. Figure 4 shows the significant parameters, inputs, and outputs for the adiabatic catalytic sections.

This numerical model was then applied to a physical configuration that uses “typical” shell and tube heat exchanger dimensions (1/8 inch inside diameter, 5 inches in length). This heat exchanger tube design is also similar to the existing adiabatic catalytic heat exchanger test data where Hutchinson examined the Para to Ortho transition (cold to warm). As Figure 5a and b show, a satisfactory step size was determined so that the model acceptably models a continuous and simultaneous catalytic and heat exchange process. The model was then exercised by comparing it to known data and test conditions from Hutchinson’s work. Figure 6 shows good agreement with these results. In addition

FIGURE 3. Overall Model Basis

FIGURE 4. Model Parameters for Adiabatic Catalyst Sections

several parametric runs using the model confirmed the very weak pressure dependence expected for the process.

Key Finding: Model shows that typical heat exchanger channel dimensions are satisfactory for pressure drop, heat exchange, and catalyst reaction rate criteria.

FIGURE 5. (a) Six Section Result (b) Sixteen Step Result

FIGURE 6. Comparison to Hutchinson Test Data

The CHEX model was used to determine what heat exchanger dimensions were needed to meet the combined constraints of pressure drop (not to large), heat transfer (small temperature difference), and conversion reaction rate (catalyst surface area). The initial modeling was done on a channel with constant wall temperature in a 1 cm channel. A second case was run where transverse cooling tubes were placed along the channel.

The results of these two simulations show that a 1 cm channel thickness will not be effective in transferring heat effectively (and therefore limiting the conversion achieved) but that reducing this dimension, even intermittently, with cooling channels had a drastic effect on the heat exchange effectiveness and therefore the conversion achieved within the CHEX channel. The result also had a dramatic effect on the amount of catalyst needed to achieve the effective conversion process within the channel. Pressure drop through the channel set the allowable flow rate and was held to typical heat exchanger values.

The results of the initial modeling set a value for a “reasonable” channel dimension of 2 mm. This size channel should allow simple “filling” of the catalyst material after channel fabrication so that any issues with high temperature brazing processes during fabrication could be avoided. A more detailed model with counter-flowing fluid channels of hydrogen and helium was

produced. This model and the simulation results are shown in Figure 7. This configuration is an effective heat exchanger and yields near equilibrium conversion conditions at the hydrogen exit and a significant temperature reduction in the hydrogen flow stream.

Key Finding: The critical sensor for measuring para/ortho make-up at cryogenic temperatures was fabricated and the performance verified.

The commercially available conductivity sensor was successfully modified to accurately measure the ortho/para composition at liquid nitrogen temperatures. The sensor housing was completely redone, especially the upper seal, which was changed from a rotating elastic seal to a face mounted indium seal.

A cryogenic test set-up used to verify the sensor performance at liquid nitrogen temperatures. Dual sensors were submerged in liquid nitrogen and the output voltage from the wheatstone bridge electrical arrangement was measured for two gasses: 1) A normal ambient hydrogen (known ortho/para gas sample composition) and 2) a helium gas sample. Figure 8 shows the results of that testing. The expected para hydrogen value is also shown on the graph to indicate the excellent accuracy expected from the instrument during CHEX testing. This figure also shows the response time of the instrument when switching from one composition gas to another.

FIGURE 7. Counter-Flow CHEX Heat Exchanger Model and Results

FIGURE 8. Test Results

Future Work

Over the next year we will complete the testing of the catalytic heat exchanger and validate the design approach for applying these heat exchangers to both the pilot plant and full-scale plant applications. We will also update both the pilot- and full-scale plant designs to refine the fabrication cost estimates.

III.12 Inexpensive Delivery of Cold Hydrogen in High Performance Glass Fiber Composite Pressure Vessels

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Start Date: October 1, 2004
Projected End Date: September 30, 2011

Accomplishments

- Successfully demonstrated process to produce subscale (3" diameter) liners from new plastic.
- Designed and analyzed (finite element) full-scale (22" diameter) vessel dome and boss using verified codes.
- Demonstrated low temperature strength of new plastic that remains elastic over temperature and pressure cycles.
- Built full-scale tooling to implement finite element analysis design (in liners of several lengths).
- Designed new specimen profile and clamp fixturing to vanquish multiple failures per specimen in cold strength tensile experiments.

Objective

- Build and test high-performance vessels for delivery truck applications.
- Test performance of glass fiber at low temperature.

Technical Barriers

This project addresses the following technical barriers from the Delivery section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

(F) Gaseous Hydrogen Storage and Tube Trailer Delivery Cost

(G) Storage Tank Materials and Costs

TABLE 1. Progress towards Meeting Technical Targets for Hydrogen Delivery in Tube Trailers

Hydrogen Delivery in Tube Trailers Characteristic	Units	2012 Target	LLNL trailer (projected)
Tube trailer delivery capacity	kg	700	1,000
Tube trailer operating pressure	psi	< 10,000	7,000-10,000
Purchased capital cost (700 kg trailer)	\$	<\$300k	\$200-300k

Introduction

Delivering hydrogen in today's low capacity compressed hydrogen tube trailers is expensive. Substantial cost reductions appear possible with development of advanced pressure vessels and a broadened range of thermodynamic conditions under which hydrogen is trucked and delivered. We have identified and confirmed synergies that promise to considerably reduce the cost of hydrogen delivery and dispensing to a vehicle. Our ongoing experimental project will test the practical feasibility of our proposed approach to inexpensive hydrogen delivery.

Approach

We are currently conducting both research and development efforts aimed at delivering hydrogen by truck. Our system concept relies on composite pressure vessels to minimize delivery cost through an optimized combination of hydrogen properties and fiber characteristics:

- **Optimization of operating pressure and temperature:** Today's hydrogen delivery technologies (compressed and liquid) are restricted to single points at extremes of the hydrogen phase diagram. Minimum cost of delivering hydrogen from centralized production (or pipelines) to filling stations can be found by exploring the entire phase diagram. Pressures and temperatures that minimize cost attain high storage density without the heavy thermodynamic penalty of hydrogen liquefaction.

Cold hydrogen at high pressure (140-200 K and up to 10,000 psi) appears most promising.

- **Use of inexpensive glass fiber:** Glass fiber is typically considered an inexpensive low performance alternative to carbon fiber. However, glass fiber strengthens as much as 100% as it is cooled down from 300 K to 140 K. Cold glass fiber maximizes delivered hydrogen per dollar by increasing trailer capacity. The combination of higher density reducing trucking labor, fuel, and capital expense more than compensates for the increased capital and energy costs of refrigeration and compression, keeping delivered cost projections below \$1/kg-H₂.

Our Fiscal Year 2009 effort is proceeding to prove that this delivery concept will work both technically and economically. Information gained from the experimental research will be applied to an ongoing full-scale hydrogen pressure vessel development project. This report describes results from the first 8 months of a three-year project.

Results

LLNL is pursuing a fundamental advance in the manufacturing of large inexpensive pressure vessels. This advance relies on the properties and manufacturing process savings implicit in a new category of plastics. These plastics are expected to form both liner and matrix of a new generation of inexpensive pressure vessels sized for low-temperature hydrogen delivery trailers. Many of the materials properties of this family of plastics have already been shown superior at very low temperatures. In collaboration with Spencer Composites, we have produced 3" diameter experimental test articles (Figure 1) to affordably determine unknown properties and improve formulations.

Tooling for full-scale liner production has just been completed. Tooling incorporates a calibrated finite element design and already measured plastic strengths sufficient to keep all structural elements well within the elastic range during independent pressure cycles to 22,500 psi (design burst pressure) and temperature cycles from 77 K to 365 K. LLNL enabled this design by performing preliminary pressure optimization in order to size vessel diameter, resulting in an economic optimum of 8,000 psi maximum expected operating pressure (MEOP) for the delivery trailer. LLNL has also made sure this full-scale design is robust enough to fit in our container design when wound with sufficient fiber to preserve safety factors of 2.25 at any MEOP from 1,500 psi to 11,500 psi. This allows the same tooling to minimize cost for stationary hydrogen storage applications (including filling station storage and renewable energy buffering).

FIGURE 1. Photographs of early test articles built and destroyed to test new matrix and liner plastic formulations and manufacturing processes. Dozens of 3" subscale pressure vessels have been built and burst tested. The figure shows a liner test article with partial graphite overwrap intended to test liner burst strength (left), a sectioned fully overwrapped vessel designed to burst at 3,000 psi with dog bone tensile test specimens cut from as-built walls (center), and a liner with 3,000-psi boss design ready for overwrapping (right).

Although we are developing a solution that can function at various temperatures and pressures, the manufactured and operating costs of this solution depend on currently unknown properties of fibers, plastics, and processed surfaces. (Overall delivery costs also depend on currently uncertain projections for the costs of refrigeration and compression, especially as functions of scale and temperature.) The single most important unknown is the fiber strength versus temperature. Even if currently available glass fiber types show only half the cold strength gain LLNL has found in legacy data [1,2], the cold glass pressure vessel delivery option minimizes delivery cost per kilogram of hydrogen.

Figure 2 shows a crucial piece of legacy data [2] that is of interest because it indicates the potential for *doubling* the strength of glass fiber composite when cooled down to ~140 K. Much of the lack of repeatability in cold glass fiber strength in the legacy data (leading to large error bars) is likely due to monolayers of water on the glass fiber surface, and our experiments have been redesigned several times to control this variable.

The highly significant unknown that we expect will depend on moisture control is glass fiber strength versus time, where we believe almost all previous data is corrupted by moisture-driven ‘corrosion’. At the moment, there is absolutely no data on “strength aging” of glass fiber at low temperature. Water vapor effects can be routinely controlled on a trailer, especially if the ambient gas (e.g. CO₂) outside the pressure vessels is chosen to maximize the sensitivity of hydrogen leak detection, and the hydrogen inside is cold enough to precipitate water in sorption “cold traps”. The lack of strength aging of much more defect-ridden plate glass

FIGURE 2. Legacy data showing the potential for great (2X) glass fiber strengthening at low temperature [2].

when tested in nitrogen, argon, or vacuum argues that our trailers can be designed for long capital life.

Measuring the cold strength effect is a challenge. If glass fiber strength indeed doubles at low temperature, there are very few materials that could stretch enough to hold on to tensile test specimens up to their failure strain. In previous experiments, we attempted to reuse a design developed at LLNL more than a decade earlier that sufficed to hold onto the strongest graphite fibers at 98% of their failure strain by gluing samples into metallic fixtures.

Our attempts to scale that design up led to high variability in the results. Special data reduction techniques (Weibull) sufficed to prove the cold strength effect in currently available glass fiber, with a measured strength gain of ~41% at liquid nitrogen temperatures. However the 10% variation in the low temperature strength was likely due to inconsistent temperature histories between cold tests. We subsequently concluded that there might be a diffusion time for water vapor in micro-cracks that considerably exceeds the thermal equilibration time. Another major concern was that many of the ‘early’ failure stresses (which were sorted out on our data reduction) were due to subsurface damage by machining a “reduced area section” and that the undamaged volume might vary considerably between specimens.

This year we have come up with major improvements in specimen and fixture design. Figure 3 shows a new set of specimen profiles that maintain a relatively long stretch of constant cross section between profiles designed to produce only one failure per specimen. We have developed a new machining process that appears to be holding 0.001” tolerances on this profile, and expect its testing will make the Weibull-method data reduction complexities unnecessary.

Figure 4 shows new specimen fixtures whose stress and strain predictions work (on paper) to hold composite rods up to ~4% strain. The replacement

FIGURE 3. Design of machined rods for a better approach to tensile testing limits the maximum shear stress experienced by the composite matrix material in a tapered neck whose profile (bottom) is much more gradual than the conventional “dog bone” test articles. The two curves shown confirm convergence of the numerical solution for this profile. These profiles, including relatively long (4”) tests sections of constant area have been successfully machined with very little surface damage using single point diamond tool (numerically controlled) milling.

of bonded fixturing with friction means that days of precisely filling fixtures with glue are replaced by minutes clamping set screws with a torque wrench. The fixtures and specimens as shown might pull out at 500,000-psi tension. However, both machining on the perpendicular axis and diluting the fiber with more matrix appear to be routine approaches to test fiber up to ~2,000,000 psi. The specimen holder has been designed to fit inside a 2.5” Dewar, and various improvements in the tensile testing apparatus have also been planned. Although we have recently discovered two ways to affordably test single fibers, these have

FIGURE 4. New test fixture under construction provides the savings in skilled labor familiar from more conventional tensile testing where clamping by friction substitutes for bonding. This approach would not work for holding the strongest composites in metal jaws, which would fail to stretch sufficiently to clamp composite at several percent strain, except that these metal jaws mount inserts of the same composite rod (visible in the photograph at right as the cross in the center of the jaws).

been rejected from our immediate plans due to their significant risks of false positive results (since many of the failure onset phenomena could be at the fiber matrix interface).

Conclusions and Future Directions

We are prototyping various novel glass composites. These test articles (rods, 3" liners, and full-scale vessels) should exhibit structural and hydrogen storage properties similar to those resulting from future mass production. Spencer Composites (and other industrial partners in a different DOE composite pressure vessel manufacturing technology award) will assist our formation of realistic production cost models. We have sufficient reason to expect that LLNL and its industrial partners can achieve new lows in hydrogen storage and delivery costs with an informed understanding of the significant technical risks that remain in the design and implementation of cold glass fiber composite pressure vessels.

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2. Metcalfe, A.G., and Schmitz, G.K., *Glass Technology*, Vol. 13, 1972. Reprinted in Lowenstein's "The manufacturing Technology of Continuous Glass Fibers," Elsevier, 1983.

FY 2009 Publications/Presentations

1. High Density Hydrogen Storage in Cryogenic Capable Pressure vessels, Salvador Aceves, Invited presentation, Purdue Hydrogen Symposium, April 2009.
2. Hydrogen-Fueled Carbon-Free Transportation, Salvador Aceves, Invited Presentation, Engineering Solutions for Sustainable Development: Materials and Resources, an international workshop organized by AIME and ASCE, Lausanne, Switzerland, July 22-24.

III.13 Reversible Liquid Carriers for an Integrated Production, Storage and Delivery of Hydrogen

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Project Start Date: February 1, 2005

Project End Date: March 31, 2011

Objectives

The overall objective of this project is to develop a conceptual design and fabricate an initial 0.1 to 1 kW prototype of a dehydrogenation reactor/heat exchange system to deliver hydrogen. Air Products is partnering in this project with PNNL, BMW and UTRC. Specifically, the project comprises the following tasks:

- Liquid phase hydrogen carrier raw materials sourcing and processing (Task 1).
- Dehydrogenation reactor development. Develop a conceptual design and fabricate an initial 0.1 to 1 kW prototype of a dehydrogenation reactor/heat exchange system to deliver H₂ (Task 2).
- Hydrogen delivery economics: conduct an economic evaluation of the delivery and storage system for the liquid carrier H₂ delivery concept (Task 3).

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Delivery section (3.2.4) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) Lack of Hydrogen/Carrier and Infrastructure Options Analysis
- (E) Low Cost, High Capacity Solid and Liquid Hydrogen Carrier Systems
- (G) Storage Tank Materials and Costs

Technical Targets

Delivery Hydrogen Carriers

Category	2005 status	FY 2012	FY 2017
Carrier H ₂ Content (% by weight)	6.2	6.6	13.2
Carrier H ₂ Content (kg H ₂ /liter)	0.054	>0.013	>0.027
Carrier System Energy Efficiency (from the point of H ₂ production through dispensing at the forecourt) (%)		70	85
Total System Cost Contribution (from the point of H ₂ Production through dispensing at the forecourt) (\$/kg of H ₂)		\$1.70	<\$1.00

Discovery of hydrogen carriers that maximize the carrier H₂ content was the subject of a separate project in H₂ storage ("Design and Development of New Carbon-Based Sorbent Systems for an Effective Containment of Hydrogen", DE-FC36-04GO14006) that was completed in Fiscal Year 2009. The objectives of the current project addresses the carrier system energy efficiency (through activities in Tasks 1 and 2) and total system cost contribution evaluation (Task 3).

Accomplishments

- Air Products has found a suitable commercial version of the test compound, N-ethylcarbazole. This material exhibited a higher rate of hydrogenation than the previously used material, which had been obtained from a laboratory materials supplier.
- PNNL performed a series of experiments with a single-channel proof-of-principle reactor operated at 210-225°C. Volatilization of the liquid is a plausible

explanation for the low productivity and low conversion, and steps are being taken to suppress volatilization.

- BMW completed initial setup of a microchannel reactor test apparatus in the second quarter of FY 2009. All pretests with an Air Products' packed-bed reactor have been successfully finished.
- UTRC modified a pre-existing system model of a coal gas-fueled solid oxide fuel cell (SOFC) plant with heat reutilization to run on hydrogen as fuel. In the modified model the anode recycle ratio replaces the steam-to-carbon constraint, allowing hydrogen operation using a relatively cool fuel inlet (<150°C).
- Continuing work at Air Products has demonstrated that stable catalyst supports can be made on microchannel reactors. Dehydrogenation is possible in these reactors at reasonable rates; however, the reactor is mass transfer limited due to the high gas flow rates at relatively high conversions. This limit is due to the flow of hydrogen at the walls, causing poor contact between the liquid and catalyst. Computational fluid dynamics (CFD) modeling of two-phase flow in a narrow channel with gas generation at the walls revealed a previously unknown circulation flow.
- BMW has supplied operating characteristics of a hydrogen-operated engine, and the team has reached agreement on a set of specifications for the laboratory reactor.
- An economic assessment of the liquid carrier approach for delivering hydrogen has been completed. Based upon our analysis, we consider the economics to be favorable, in the range of \$0.85 – \$4.50/kg of H₂ delivery cost using N-ethylcarbazole as a test molecule. Additional work tailoring the characteristics of the carrier material and catalyst system should allow the cost of delivered hydrogen to fall in the lower end of this scale and thus should compare favorably to the DOE targets.

Introduction

An alternative approach for the large-scale delivery of hydrogen from large central production facilities to forecourt users (e.g. customers at fueling stations) is the use of reversible carrier media that liberate hydrogen at the point of use. The hydrogen can be obtained from the carriers at the fueling station for subsequent dispensing to vehicles. Ideally, the carrier can be used for hydrogen storage onboard the vehicle and hydrogen can be released on demand for vehicle propulsion. Primary advantages of carrier-based distribution of hydrogen potentially include lower capital and operating costs, higher efficiency, and enhanced safety.

This project is directed at providing the reactor technology, integration of reactor designs with vehicle and stationary power sources, and economic analysis for a liquid phase carrier that will enable an integrated delivery and storage of hydrogen, while meeting the DOE targets for hydrogen storage density and delivery efficiency. Due to funding issues in previous years, the subcontracts were not executed with PNNL, UTRC, and BMW until late FY 2008/early FY 2009. Therefore, the reported results from these subcontractors represent less than one year of effort.

Approach

Efficient dehydrogenation of the liquid carrier is integral to the viability of this concept for hydrogen storage and delivery. Microchannel reactor technology was identified at an early stage as a promising reactor architecture for carrier dehydrogenation. The technical approach is to develop catalyst substrates that are able to effectively segregate liquid from gas and release the hydrogen as it is generated from the catalyst structure. PNNL is a leader in the development of microchannel reactors and in collaboration with Air Products and BMW, several generations of “proof-of-principle” reactors are under development at PNNL. After initial testing at PNNL, the reactors will be used for integration studies at BMW. BMW's objective is to evaluate the integration of liquid carrier storage systems with hydrogen internal combustion engines (H₂-ICE). This will define certain configurations of integrated systems, determine the preliminary requirements to guide reactor development and allow modeling of more complex scenarios to show overall system performance needs. Additional reactor testing will occur at BMW. Data from the reactor testing will be used by UTRC for the modeling of stationary and mobile fuel cells. UTRC's objective is to evaluate the integration of liquid carrier storage systems with fuel cell systems. This will define certain configurations of integrated systems, determine the preliminary requirements to guide reactor development and allow modeling of more complex scenarios including transient operation. Air Products is supplying the necessary liquid carrier and conducting an economic evaluation of the use of liquid carriers for hydrogen distribution.

Results

Task 1. Liquid Phase Hydrogen Carrier Raw Materials Sourcing and Processing

Air Products is responsible for providing hydrogenated N-ethylcarbazole for testing. The team estimates that about 150 gallons of material will be needed for the entire project. We have located a supplier for N-ethylcarbazole offering a commercial-

scale supply. This new raw material was tested in both 50 ml and 1 liter reactors. The material from the new supplier hydrogenates faster than the standard material. We found that material from our initial supplier contained a small amount of chloride, which slowed down the reaction.

A single lot of 200 kg of N-ethylcarbazole has been purchased from the supplier and we have begun a campaign to hydrogenate the entire lot, thereby building an inventory of liquid carrier that should support the reactor testing for the duration of the project.

Task 2. Dehydrogenation Reactor Development and Systems Integration Modeling

PNNL: Testing was started in the first quarter of FY 2009 on compact microchannel dehydrogenation reactors that are able to achieve high catalyst productivity in the process of generating hydrogen from liquid organic hydrogen carriers (LOHCs). A method was developed for coating Pt/Al₂O₃ (or Pd/Al₂O₃) catalyst on porous substrates for testing in a single-channel microchannel reactor. Uniform coating of the wick structure at a loading of 10 mg/cm² with good adhesion was achieved. Temperature programmed reduction was performed on the calcined slurry of Pt/Al₂O₃ catalyst in order to determine the reduction temperature needed to fully reduce the Pt. The results indicated that reduction at 200-220°C is sufficient to reduce the catalyst.

A single-channel test reactor was selected and an apparatus was built for testing catalytic structures. The reactor was intended to perform phase separation and produce separate liquid effluent and hydrogen gas streams. Consequently, initial tests were conducted at room temperature with the hydrogen carrier liquid and nitrogen to determine the operation conditions under which complete phase separation could be maintained. Flow-through tests with the initial catalyst structure were conducted with perhydro-N-ethylcarbazole flowing at 0.1 ml/min and 20 sccm N₂ flow.

Benchmark experiments were conducted to evaluate the performance of the microchannel reactor setup during the dehydrogenation of perhydro-N-ethylcarbazole. The experiments were performed at a liquid flowrate of 0.1 ml/min at 215°C. The conversion obtained was about 18%, and the H₂ flowrate was 14 sccm. In these initial experiments, there was entrainment of liquid in the hydrogen gas and vice versa, indicating the catalyst structure was not effectively releasing the hydrogen being generated, which also resulted in inefficient use of the catalyst.

Additional testing of a single-channel test reactor encountered unexpected difficulties in maintaining good segregation of the liquid in the wicks. Although the perhydro-N-ethylcarbazole remained in the wick while

flowing through the reactor at low temperature (e.g., 25°C), as shown on the left of Figure 1, droplets formed in the vapor space when the temperature was increased to the range typically required to release hydrogen, as shown on the right of the figure. The explanation that was eventually supported by testing was that heating from the bottom with the sapphire window on top – even with the window covered in insulation – creates temperature gradients sufficient to cause Marangoni instability in the vapor-liquid interface. This instability causes stable droplets to form in the vapor space. The temperature gradients have been dissipated by heating the window, and the reactor can now be operated with good phase separation at temperature.

Performance targets have been set for the single-channel reactor shown in Figure 1. The objective is to generate 0.65 slpm of H₂ targeting a catalyst loading of 1 mg Pt/cm². So far, wick structures have been developed with 24-40% of the target catalyst loading. A series of experiments has been performed with the single-channel proof-of-principle reactor operated at 210-225°C. Various wicks have been used over a range of liquid feed rates and suction pressures on the wick structure. The total hydrogen production has been typically at 2% of target or less, and the catalyst productivity has been at 12% or less. Liquid conversion has also been in the 1.5-5% range. Volatilization of the liquid is a plausible explanation for the low productivity and low conversion. In several experiments, particularly at the lower liquid feed rates and higher suction pressures on the wick, the wicks appear to be dry, even though the siphon on the wick is maintained. The test stand was originally set up to collect both the liquid and vapor streams in the same vessel, which precluded knowing what fraction of the liquid is volatilized. After the test apparatus was modified, a recent test revealed that 70% of the liquid is being condensed from the vapor stream. Steps are now being taken to suppress volatilization. Concepts are also being developed to convert the vapor to generate additional hydrogen. Initial testing of these concepts has yielded promising results.

FIGURE 1. Microchannel reactor with sapphire window illustrating droplet formation when increasing from 25°C (left) to 210°C (right).

FIGURE 2. Reactor Testing Apparatus Constructed in BMW Laboratories

BMW: BMW has successfully finished the initial set up of an apparatus for testing microchannel reactors (Figure 2). The test rig consists of a combination of off-the-shelf Swagelok parts in combination with purpose-built components. As measurement hardware, existing test equipment for automotive test drives is used. National Instruments' DIAdem and ETAS INCA are used as software. The first hydrogen was generated using a packed-bed reactor supplied by Air Products. After initial testing of the system, a planned upgrade added test equipment such as flow meters, temperature controllers and pressure gauges. Additionally, there are plans for in situ direct gas analysis of the produced hydrogen. BMW has transferred the existing spreadsheet-based calculations to 1-dimensional simulation software Matlab-Simulink and added Air Products' kinetic modeling data to the model.

BMW has supplied operating characteristics of an H₂-ICE, and based on these data, the team has reached agreement on a set of specifications for the laboratory reactors. Measurements of basic material properties at BMW's chemistry lab have been finished.

UTRC: UTRC has obtained and reviewed models for fuel cell-based systems from UTRC and UTC Power, namely:

- UTRC system model for an on-board complex compound hydride based hydrogen storage system coupled to a proton exchange membrane fuel cell (PEMFC). For on-board hydrogen generation, the operation temperature of a PEMFC is too low for integration with the LOHC dehydrogenation reaction, but it could be used for preheating the carrier, including producing and maintaining a liquid state.
- UTC Power steady-state system configuration and model results for phosphoric acid fuel cell stationary plants running on reformed natural gas and other fuels.

FIGURE 3. Preliminary Baseline System Model for Liquid Carrier Dehydrogenation

- UTRC steady-state model for an SOFC stationary plant running on reformed natural gas.

A preliminary baseline system configuration was constructed (Figure 3). For this system, the energy of the dehydrogenation process is obtained by burning a fraction of the produced hydrogen. A heat transfer fluid is used to convey that additional energy back to the dehydrogenation reactor in a manner which would produce a high degree of temperature uniformity. This preliminary configuration is similar to a subsystem of a layout studied by Argonne National Laboratory [1]. This system was subsequently identified and will be used as a guideline in the near term. A change being considered is the addition of a loop for preheating the liquid carrier using the coolant exiting the fuel cell stack.

As a stepping stone to full integration of a model of the dehydrogenation reactor with a stationary SOFC power plant, a pre-existing UTRC system model of a coal gas-fueled SOFC plant with heat reutilization was modified to run on hydrogen as fuel. The previous system model was designed to prevent coking by imposing a certain steam-to-carbon ratio at the anode entrance. In the modified model the anode recycle ratio replaces the steam-to-carbon constraint, allowing hydrogen operation using a relatively cool fuel inlet (<150°C). An effect of the transition to pure hydrogen fuel is that the net-endothermic process of steam reforming plus water-gas shift at the cell is now absent. The loss of this cooling process is compensated by increased cathode flow rate.

Air Products: Continuing work at Air Products uses CFD to understand the multiphase flow conditions in catalyst-coated microreactors. Previously, we calculated that for the dehydrogenation rates necessary to achieve complete dehydrogenation, the gas flow is very high, and a layer of hydrogen is found near the catalyst walls. This layer of gas prevents the liquid reactant from contacting the catalyst on the walls, thereby causing low catalyst efficiency. This phenomenon of gas building on the walls occurs because the gas-to-liquid volumetric ratio is very high, and the hydrogen flow has considerable

momentum because of the high velocity. The modeling results show that gas is found at the wall and that the strong gas flow creates a liquid recirculation within the micro channel, which can lead to reverse flow at the exit. This secondary flow was unexpected. The liquid flow tends to eliminate any mass transfer resistance in the liquid; however, the gas flow at the wall leads to catalysis inefficiency, as discussed previously.

Kinetic models are needed to assess the performance of wash-coated and other types of catalysts, as well as judge the efficiency of the new reactor designs. Therefore, kinetic models for both Pt and Pd catalysts have been developed. The kinetic model for the Pd catalyst was improved from previous models by considering the first two steps of the dehydrogenation reactions as irreversible and the final step as reversible. For the Pt catalyst, all three reactions were modeled as irreversible. We were able to obtain good fits to the data from previously reported large-scale batch experiments (Figure 4).

Microchannel reactor testing was accomplished by engineering an annular reactor from 5/8 inch diameter iron/chromium metal tubing and inserting a 3/8 inch diameter thermocouple into the center of the tube. The resulting annulus was 0.7 mm in width with a diameter of 10.9 mm. The catalyst wash coat was located on the inside of the outer tube. The reactor length was 12 inches for testing of Pd catalyst and 10 inches for the Pt catalyst.

Two sets of experiments were performed for the reactor with the Pd catalyst. In the first set of experiments, the feed flow rate was varied, and the hydrogen flow rate was noted. Reactor performance was similar to previous single channel reactor experiments. Repeat runs at the same feed rate showed no evidence of earlier catalyst flaking problems found with a stainless steel, alumina-coated reactor. The second set of experiments was performed to see if mass transfer issues were present. Typically this test involves changing the amount of catalyst in the reactor. In our case, the reactor tube was cut in half, providing two 6-inch-long reactors. Each of the two reactors had half the catalyst of the previous reactor. The kinetic model discussed above was used to analyze the data. Typical results from both sets of experiments are shown in Table 1.

Results for the shorter reactor are the average of the results for the two halves of the larger reactor. The results of these individual, half-length reactors were similar, indicating that a stable catalyst coating had been achieved. Previously reported batch reactor experiments have shown a productivity of about 2 gm H₂/gm Pd/min in the range of 40-90% conversion. However, because the run was not isothermal, the only way to compare the catalyst efficiency was to use a kinetic rate model. For a feed rate of 0.25 ml/mi, a flow rate of hydrogen was 39 sccm using the full-length reactor. The

FIGURE 4. Figure showing data collected using an annular microchannel reactor with Pt catalyst and the fit to a kinetic expression developed using batch reactor dehydrogenation.

simulation shows that this flow rate could be achieved by ~0.44 milligrams of Pd at 100% efficiency. The full-length reactor contained approximately 4 mg of catalyst. Thus, catalyst efficiency was only about 11%.

TABLE 1. Reactor Experiment Results

Reactor Length (cm)	Liquid Feed Rate (cc/min)	H ₂ Flow Rate (sccm)	Conversion %	Rate/gm Pd (gm H ₂ /gm Pd/min)	Temp. (°C)
30.5	0.10	23	38	0.5	248
30.5	0.25	38	25	0.8	252
30.5	0.40	50	20	1.1	251
30.5	1.00	75	12	1.7	256
15.25	0.11	21	34	0.9	248
15.25	0.25	26	17	1.2	248
15.25	0.40	33	14	1.5	248
15.25	1.00	55	9	2.5	253

Catalyst efficiency is a function of the catalyst manufacturing variables, e.g., dispersion, and hydrodynamic effects. If all of the efficiency loss is due to manufacturing, we would expect that the half-length reactor would have about half the effective catalyst, i.e., 0.22 mg effective catalyst, and the hydrogen flow rate would be about 19 sccm. However, the measured flow rate for the half-length reactor was 26 sccm. Thus, catalyst efficiency is higher for the shorter reactor than for the longer reactor. Clearly, flow effects must be important in determining catalyst efficiency as well as manufacturing effects. Thus, the experimental evidence seems to agree with the CFD prediction that the high flow of hydrogen decreases flow efficiency.

Task 3. Hydrogen Delivery Economics

A detailed economic analysis was completed in the third quarter of FY 2009 and has been submitted as a report to DOE. Based upon our analysis, we consider the H₂ liquid carrier economics to be favorable, in the range of \$0.85 – \$4.50/kg H₂ delivery cost with respect to current DOE targets, provided that certain performance and cost targets can be achieved for the liquid carrier, hydrogenation catalyst productivity, liquid carrier loss rate and dehydrogenation efficiency. To be specific, we recommend lowering liquid carrier cost to under \$10/gallon, lowering carrier melting point, reaching catalyst productivity targets exceeding 1,000,000 kg liquid carrier processed/kg catalyst metal (close to existing hydro-desulfurization catalysts), reducing carrier loss rate to less than 2% per year and investing in understanding cost-performance issues around fuel cell reactor heat integration to enhance predictability. Dehydrogenation reactors need to be investigated further alongside their integration performance with the fuel cell over dynamic conditions encountered on-board automobiles. Performing more analyses around these factors will eliminate significant uncertainties surrounding the liquid carrier concept.

Conclusions and Future Directions

- Initial results from the development of microchannel reactors have confirmed that effective gas/liquid separation is critical to achieving high conversion of the hydrogenated liquid carrier.
- Experimental results and CFD modeling has suggested that high gas flow rates represent a challenge due to drying of catalyst surfaces. While the first generation of microchannel reactors developed at PNNL has largely overcome these issues, the vaporization of the hydrogenated liquid carrier has presented new challenges. Two new types of microchannel reactors will be evaluated in the remainder of FY 2009 to address low conversion due to the liquid carrier vaporization.

- Ramping up of reactor testing capability at BMW has been completed. Final testing of the testing apparatus will be completed using annular tube microchannel reactors. The testing of proof-of-principle reactors constructed at PNNL is expected to commence within FY 2009.
- Additional high-level system evaluation of reactor systems with H₂-ICEs will be performed.
- Complete N-Ethyl Carbazole-specific elements for the system modeling library.
- Develop a high-level model module to represent reactor performance.
- Perform steady-state evaluation of at least two system configurations.

Special Recognitions & Awards/Patents Issued

1. U.S. Patent 7,485,161; Dehydrogenation of liquid fuel in microchannel catalytic reactor (issued Feb. 3, 2009).

FY 2009 Publications/Presentations

1. Potentiale von alternativen Wasserstoff-Speicherungstechnologien ("Potential of alternative Hydrogen Storage Technologies"), von Wild, Jürgen et al., 6. VDI-Tagung "Innovative Fahrzeugantriebe", November 6th and 7th 2008, Dresden, Germany, published in: "VDI-Berichte/VDI-Tagungsbände, Sachgebiet: Fahrzeug- und Verkehrstechnik," Volume Nr. 2030, 520 pages, year 2008, Title: "Innovative Fahrzeugantriebe 2008 inkl. CD-ROM", ISBN: 978-3-18-092030-6.
2. "Reversible Liquid Carriers for an Integrated Production, Storage and Delivery of Hydrogen", Bernie Toseland and Alan Cooper, U.S. Department of Energy HFCIT Annual Merit Review, May 2009.

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III.14 Design of Advanced Manufacturing Technologies for Low Cost Hydrogen Storage Vessels

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Working Partners:

- Quantum Technologies, Inc. (Quantum)
- Boeing Phantom Works (Boeing)
- Lawrence Livermore National Laboratory (LLNL)

Project Start Date: October 1, 2008
Project End Date: September 30, 2011

Objectives

The project objectives are to develop new manufacturing methods for lower cost Type IV hydrogen storage vessels and to quantify the durability of tank liner materials under high hydrogen pressure cycling. PNNL is collaborating with Quantum, Boeing, and LLNL to optimize composite tank manufacturing methods. PNNL's task objectives are to:

- Analyze the manufacturing costs of advanced manufacturing methods for lower cost hydrogen storage vessels.
- Quantify hydrogen induced blistering of polymer liner materials as a function of material parameters (viscosity, solubility, crystallinity) and operating conditions (pressure, temperature, and decompression rate).

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) System Weight and Volume
- (B) System Cost
- (D) Durability/Operability

(G) Materials of Construction

(M) Lack of Tank Performance Data and Understanding of Failure Mechanisms

2010 Technical Targets

- A. System Weight and Volume = 2 kWh/kg (6 wt%), 1.5 kWh/L
- B. System Cost = \$4/kWh
- D. Durability/Operability = 1,000 filling cycles.
- G. Materials of Construction = resistant to hydrogen permeation and blistering
- M. Lack of Tank Performance Data and Understanding of Failure Mechanisms = understand the fundamental mechanisms of hydrogen permeation in polymer liner materials.

Analyzing the costs of advanced composite tank manufacturing compared to the baseline filament winding process will quantify how new manufacturing methods could improve the composite efficiency and reduce the weight and volume and cost of carbon fiber composite materials. The total manufacturing cost model will weigh material cost savings against modified processing costs.

This project is also developing a strong fundamental knowledge base on hydrogen/polymer interactions necessary for the materials selection for such vessels. This will help to obtain the DOE targets of increased durability and operability for on-board hydrogen storage.

Accomplishments

- Developed system for testing hydrogen/polymer compatibility under hydrogen pressures up to 5,000 psi and temperatures up to 200°C.
- Demonstrated hydrogen damage (surface blisters) occurs in amorphous polymers and is strongly a function of temperature. Testing of crystalline and semi-crystalline polymers to follow.
- Developed a thermal gradient stage for in situ thermal combinatorial testing of hydrogen degradation under high pressure hydrogen atmospheres.
- Identified and prioritized the significant manufacturing costs (considering process steps, materials, equipment, factory space, labor) for compressed hydrogen storage tank.
- The baseline filament winding (FW) process flow is defined. Material processing speeds and hardware

needs are being evaluated to best integrate the automated fiber placement (AFP) method into a hybrid FW + AFP manufacturing process.

Introduction

PNNL is collaborating with Quantum, Boeing, and LLNL to develop new manufacturing methods for lower cost Type IV hydrogen storage vessels and to quantify the durability of tank liner materials under hydrogen pressure cycling. The work began in October 2008 and it directly targets minimizing the weight, volume and cost of tanks plus the durability of tank materials. The durability and lifetime of hydrogen composite tanks is necessarily strongly influenced by the hydrogen degradation of the polymer liner material in direct contact with the high pressure hydrogen. While hydrogen degradation mechanisms are well known for metallic systems including blistering and embrittlement, relatively little is known about the effects of hydrogen on polymer systems. To answer this knowledge gap PNNL has carried out experimental investigations of the degradation of polymer materials in a high pressure hydrogen environment as a function of temperature. An analysis of our preliminary findings indicates that hydrogen blistering is the predominant degradation mechanism in polymer systems and is a strong function of temperature (viscosity) and crystallinity. PNNL hopes to use this and future data to build a predictive model of polymer behavior in high pressure hydrogen to address durability and lifetime issues. PNNL is also developing detailed manufacturing cost models for Quantum's baseline FW process and a hybrid process that will use the Boeing AFP method to improve the fiber placement efficiency in the FW process.

Approach

PNNL investigated the effects of high pressure hydrogen as a function of temperature on the degradation of polymer films with the goal of developing a model to understand hydrogen degradation of the polymer liner in high pressure composite tanks. Most polymer liner candidates are semicrystalline material, consisting of amorphous and crystalline regions. In order to separate the effects of hydrogen in the two different regions PNNL has decided to investigate amorphous, crystalline, and semi-crystalline materials separately in order to better develop a model for degradation. At this stage PNNL has extensively explored the simplest case – amorphous polymers – and has done some preliminary studies on crystalline polymers. Additional studies on all three systems are planned.

Polymer films with ultra-low roughness surfaces are exposed to high pressure hydrogen while mounted on a thermal gradient stage developed at PNNL for this project for in situ combinatorial studies of hydrogen degradation over a large temperature range (see Figure 1 a, b). Samples are typically exposed to high pressure hydrogen for 1 day and undergo controlled decompression under the elevated temperature gradient. Since these are thin films, 1 day is sufficient for hydrogen concentration saturation. Samples are then evaluated with optical microscopy for possible surface degradation. The low roughness aids in observing blistering.

The current FW process will be used as the baseline manufacturing cost for comparison with the advanced processing method. The goal of the advanced processing method is to increase the efficient use of the fibers in

FIGURE 1. (a) Photograph of the high pressure autoclave (center) and thermal gradient control box (right). The high pressure autoclave is capable of hydrogen atmospheres up to 5,000 psi and temperatures of up to 300°C. (b) The thermal gradient stage consists of a heater at one end and a large heat sink tied to the autoclave at the opposite end. The sample sits on top of the bar and is subjected to a linear thermal gradient of up to 50°C over 3 inches. Resistance temperature detection devices allow in situ measurement of the temperature at several locations. The maximum temperature of the hot end is approximately 200°C.

the composite and thus reduce the amount of composite material needed for a given burst pressure. The challenge is to accurately place the fibers in the optimum directions while doing it quickly and with limited additional machinery such that the alternate manufacturing costs do not exceed the material savings cost.

Results and Discussion

PNNL has observed extensive micron-scale surface blistering (see Figure 2) in amorphous (polystyrene) where blister size and density varies strongly with temperature. For the amorphous samples blistering only occurred at temperatures above the glass transition temperature (transition from glassy solid to viscoelastic liquid). Note that most semi-crystalline polymer liner candidates have glass transition temperatures below room temperature which allows them to have superior mechanical properties, including ductility. This temperature dependence is likely due to two main effects. The first effect is that of hydrogen solubility. Hydrogen solubility in polymers has been shown to be strongly a function of free volume which increases as the polymer is heated. Thus the solubility should increase with increasing temperature. The second effect is that of viscosity. The polymer viscosity changes over many orders of magnitude with heating past the glass transition as the polymer goes from a glassy solid to a viscoelastic liquid. Thus mass flow is markedly enhanced at temperatures above the glass transition and more damage is expected to occur. Figure 3 shows that both the blister size and density of blisters increases with increasing temperature (decreasing viscosity).

Preliminary tests of crystalline films with a nearly identical polymer (isotactic vs atactic polystyrene of identical molecular weight) over the same temperature range shows no observable blistering. This is thought to be due to the comparatively decreased free volume of

FIGURE 2. Micron-Scale Blisters in an Amorphous Polystyrene Film

FIGURE 3. Histogram data of blister radius from image analysis of optical micrographs for 150°C and 180°C. Note the data indicates larger blisters for the higher temperature. The second peak at smaller size for 180°C is likely due to subsurface blisters, though further investigation is warranted.

the crystalline polymer as compared with the amorphous case. The hydrogen solubility should be lower and the material stiffer and more resistant to damage from hydrogen. The information from these preliminary examinations and from future work will help to build a model to predict the durability and lifetime of polymer liner materials in high pressure hydrogen.

PNNL's cost modeling efforts to date have focused on identifying the significant cost factors for inclusion in the models. This includes the materials, equipment, factory space, and labor costs for each processing step. The material and labor costs for Quantum's baseline FW process have been defined as the baseline. Material processing speeds and hardware needs are being evaluated to determine how to best integrate the AFP method into a hybrid FW + AFP manufacturing process. During the first year, much progress has been made by Quantum and Boeing to identify compatible materials and processing scenarios for the combined FW + AFP process. An initial cost model comparison of the FW and the hybrid FW + AFP method will be completed by the end of Fiscal Year 2009.

Conclusions and Future Directions

- Hydrogen degradation of amorphous polymers does occur in the form of surface blistering.
- This blistering damage increases with increasing temperature above the glass transition temperature of the polymer.
- Blistering appears not to occur for purely crystalline materials.

- The cost models are progressing and a comparison of the baseline and advanced manufacturing methods will be completed.

PNNL hopes to continue this work to develop a model for polymer durability in a high pressure hydrogen environment by addressing the following issues:

- What is the specific temperature/viscosity dependence on blistering?
- Develop an analytical model to describe this.
- How can this be incorporated into a semi-crystalline system composed of amorphous and crystalline regions?
- What is the role of impurities on hydrogen damage?

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III.15 Design and Development of High Pressure Hydrogen Storage Tank for Storage and Gaseous Truck Delivery

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Contract Number: DE-FG36-08GO18062

Project Start Date: July 1, 2008

Projected End Date: June 1, 2011

TABLE 1. Technical Targets

Hydrogen delivery Targets	ISO Container with four 3,600 psi tanks (Fiscal Year 2009 work scope)
\$500/kg stored hydrogen by FY 2010	The current ISO assembly, with four tanks installed, can store approximately 600 kg of compressed hydrogen gas at 3,600 psi. It is estimated that the initial cost will be \$675-750/kg of hydrogen depending on market conditions.
Volumetric capacity 0.03 kg/liter by FY 2010	The baseline tank has a capacity of 150 kg hydrogen in a volume of approximately 8,500 liters, achieving a performance of about 0.018 kg/liter. This performance measure can be increased to 0.024 kg/liter by increasing the service pressure to 5,000 psi.
Tube trailer delivery capacity 700 kg by FY 2010	The current ISO assembly, with four tanks installed, will contain about 600 kg of hydrogen. This can be increased to about 800 kg by increasing the service pressure to 5,000 psi.

Project Objective

The objective of this project is to design and develop the most effective bulk hauling and storage solution for hydrogen in terms of:

- Cost
- Safety
- Weight
- Volumetric Efficiency

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Delivery section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

(C) Cost

(F) Transport Storage Costs

Technical Targets

This project will focus on the design and qualification of a 3,600 psi tank and an International Organization for Standardization (ISO) frame system in the first year to yield a storage capacity solution of approximately 8,500 L of water. The technical targets of the project are presented in Table 1.

Accomplishments

- Successful completion of design and partial qualification of a 3,600 psi tank. Qualification testing included:
 - Strength testing (burst and pressure cycling).
 - Environmental testing (exposure to environmental fluids, extreme temperatures, and high temperature creep).
 - Durability testing (flaw tolerance per ISO 11439 and penetration).
 - Other special tests (blow down, accelerated stress rupture, and leak-before-burst).
- Successful completion of design and partial qualification of ISO frame capable of holding four 3,600 psi tanks with a combined capacity of 600 kg of hydrogen. In addition to the structure, a system for loading, unloading, and pressure relief has been designed and implemented.

Introduction

Hydrogen holds the long-term potential to solve two critical problems related to energy use: energy security and climate change. The U.S. transportation sector is almost completely reliant on petroleum, over half of which is currently imported, and tailpipe emissions remain one of the country's key air quality concerns.

Fuel cell vehicles operating on hydrogen produced from domestically available resources would dramatically decrease greenhouse gases and other emissions, while also reducing our dependence on oil from politically volatile regions of the world.

Successful commercialization of hydrogen fuel cell vehicles will depend upon the creation of a hydrogen delivery infrastructure that provides the same level of safety, ease, and functionality as the existing gasoline delivery infrastructure. Today, compressed hydrogen is shipped in tube trailers at pressures up to 3,000 psi (about 200 bar). However, the low hydrogen-carrying capacity of these tube trailers results in high delivery costs.

Hydrogen rail delivery is currently economically feasible only for cryogenic liquid hydrogen; however, almost no hydrogen is transported by rail. Reasons include the lack of timely scheduling and transport to avoid excessive hydrogen boil-off and the lack of rail cars capable of handling cryogenic liquid hydrogen. Hydrogen transport by barge faces similar issues in that few vessels are designed to handle the transport of hydrogen over inland waterways. Lincoln Composites' ISO tank assembly will not only provide a technically feasible method to transport compressed hydrogen over rail and water, but a more cost and weight efficient means as well.

Approach

In this project, Lincoln Composites will design and qualify a large composite tank and ISO frame that can be used for storage and transport of compressed hydrogen gas over road, rail or water.

The baseline composite tank will have a 3,600 psi service pressure, an outer diameter of 42.8 inches, and a length of 38.3 feet. The weight of this tank will be approximately 2,485 kg. The internal volume is equal to 8,500 liters water capacity, and will contain 150 kg of compressed hydrogen gas. The contained hydrogen will be approximately 6.0 percent of the tank weight (5.7 percent of the combined weight).

Four of these tanks will be mounted in a custom-designed ISO frame, resulting in an assembly with a combined capacity of 600 kg of hydrogen. An ISO frame and tank mounting system will also be designed to accommodate up to four (4) of these tanks, as illustrated in the solid-model geometry shown in Figure 1.

Installing the compressed hydrogen tanks into an ISO frame offers a benefit of having one solution for both transportable and stationary tanks. This decreases research and development costs as well as the amount of infrastructure and equipment needed for both applications.

FIGURE 1. Solid-Model Geometry of the TITAN ISO Frame System

The large size of the tank also offers benefits. A limited number of large tanks is easier to package into the container, and requires fewer valves and fittings, which results in higher system reliability and lower system cost. The larger diameter also means thicker tank walls, which will make the tank more robust and damage tolerant.

During the course of the project, Lincoln Composite will evaluate different tank dimensions, safety factors, service pressures, and other factors in order to optimize the performance of the tank related to the DOE project goals. The ISO mounting frame will also be designed to existing standards and the ISO assembly will be tested for compliance to rigorous transportation standards.

Results

Design and Manufacture of 3,600 psi Tank

The design of the 3,600 psi pressure vessel architecture has been completed using finite element analysis to find a composite solution that resolved the internal pressure requirements and expected external loads. This design was translated into a manufacturing process that addresses the feasibility of tank production. A significant challenge has been the scale up of our standard manufacturing processes and equipment, including the liner weld fixture shown in Figure 2. Several development design verification test (DVT) units were fabricated and pressurized until burst to validate the proposed manufacturing process and design.

With the completed design and working manufacturing process, several additional tanks were fabricated and tested to address optimizing

FIGURE 2. Development of the Manufacturing Processes for the 3,600 psi TITAN Tank has Required Scale Up of All Manufacturing Processes and Equipment

manufacturing issues and minimizing production expenses. One of the units was fabricated and tested to ensure the highest risk associated with material availability could be addressed. By ensuring multiple sources of supplied material, more leverage is available during procurement and lower production costs can be realized. Another unit was fabricated to help establish confidence with migrating to a design having a higher margin of safety. Both of these units were subjected to a proof cycle and hydraulic burst test. The results of the testing met the expectations predicted by design.

Two additional tanks were fabricated and subjected to a proofing cycle and successfully passed but are waiting further hydraulic burst testing. One of these tanks was fabricated to study the effects of allowing certain manufacturing perturbations into the process that would reduce production costs of the tanks. The other DVT unit was fabricated using a modified material configuration to test the feasibility of a higher performance vessel and to enhance its cosmetic appearance.

Qualification of 3,600 psi Tank

Due to the tank's geometry and construction there are no published standards that can be used to directly qualify the product to. There do exist, however, standards to qualify small pressure vessels of similar construction. These standards were reviewed for input to determine the appropriate requirements that would apply to a vessel of this geometry and construction and include:

- ISO 11439, gas cylinders – High Pressure Cylinders for the On-Board Storage of Natural Gas as a Fuel for Automotive Vehicles
- ISO 11119-3, Gas Cylinders of Composite Construction (fully wrapped non-metallic liners)

- American National Standards Institute/Canadian Standards Association Natural Gas Vehicle 2-2007, American National Standards for Natural Gas Vehicle Fuel Containers
- American Society of Mechanical Engineers (ASME) Code Case in Work/ASME BPV Project Team on Hydrogen Tanks and Section X

Some of the qualification tanks that were fabricated have successfully completed and passed their respective test requirements. These include two tanks that were hydraulically burst and another tank that was subjected to ballistic penetration. Several others have passed a proofing test and will be used to qualify the ISO frame hauling system and additional testing such as:

- Cycle testing (ambient, leak before burst, and extreme temperature).
- Flaw tolerance per ISO 11439.
- Blow-down.

Design and Manufacture of the ISO Frame

An ISO frame has been designed to hold four large hydrogen carrying pressure vessels. The frame was modeled in FEMAP (a computer aided design independent pre- and post-processor for engineering finite element analysis, marketed by Siemens) and analyzed with NX Nastran using 28 load cases, including all conditions described in specification ISO 1496-3. This effort was contracted out to a professional engineering firm and a documented stress analysis report has been delivered.

The ISO frame construction was constructed by a metal fabricator having experience with this size of structure and shipped to our facility in February 2009. Tank and plumbing installation was completed as well as the installation of a fire protection/pressure relief system. The completed assembly is shown in Figure 3. The

FIGURE 3. Final Assembly of TITAN ISO Frame System

American Bureau of Shipping has conducted a Hazard Identification Analysis study on the design concept and the identified risks have been mitigated.

Qualification of the ISO Frame

The ISO container was recently sent out for qualification testing with the following results:

- Structural testing completed.
- Rail impact test completed.
- Bonfire test is scheduled for August.

The ISO frame qualification test unit is shown leaving our manufacturing facility in Lincoln, NE in Figure 4. Upon completion of remaining qualification tests, the American Bureau of Shipping has agreed to certify the entire ISO container assembly including tanks and pressure relief system.

FIGURE 4. TITAN ISO Frame System Departs for Final Qualification Testing

Conclusions and Future Direction

Proposed objectives for the first budget period of this project are very close to being achieved. By the end of summer 2009, all qualification testing will have been completed. The results of the completed qualification testing are very promising. Additional testing done earlier has shown the feasibility of pursuing a 5,000 psi configuration to better meet the DOE future hydrogen storage goals.

The plan forward for completing the qualification of the 3,600 psi tank involves:

- Completion of sub-scale testing activity.
- Completion of sub-length cycle testing activity.
- Completion of full-scale cycle testing activity.

The plan forward for completing the qualification of the ISO frame involves completion of the bonfire test. Both qualification activities are expected to be completed by the end of summer 2009. Upon completion a Go/No-Go decision will be made to pursue the development of the 5,000 psi tank design.

III.16 Composite Technology for Hydrogen Pipelines

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Start Date: January 2005
Projected End Date: Project continuation and
direction determined annually by DOE

Technical Targets

The long-term project objective is to achieve commercialization and regulatory acceptance of FRP pipeline technology for hydrogen transmission and distribution. Accordingly, the project tasks address the challenges associated with meeting the DOE hydrogen delivery performance and cost targets for 2017 [1]:

- Transmission pipeline total capital cost: \$490K per mile
- Distribution pipeline total capital cost: \$190K per mile
- Hydrogen delivery cost: <\$1.00/gge
- Transmission and delivery reliability: Acceptable for H₂ as a major energy carrier
- Hydrogen pipeline leakage: <0.5% (leakage target is currently under review by the Delivery Tech Team)

Objectives

- Investigate the use of composite pipeline technology (i.e., fiber-reinforced polymer [FRP] pipelines) for transmission and distribution of hydrogen, to achieve reduced installation costs, improved reliability and safer operation of hydrogen pipelines.
- Evaluate current composite pipeline liner materials with respect to their performance as a hydrogen barrier, consider the hydrogen permeabilities of the materials to determine the degree of improvement (if any) that is necessary, and propose a path forward based on the available liner materials and modifications or treatments.
- Assess joining methods for composite pipelines.
- Determine integrated sensing and data transmission needs pipelines to provide health monitoring and operational parameters; report on state-of-the-art in structurally integrated sensing and data transmission.

Accomplishments

- Pipeline materials compatibility testing:
 - Completed long-term hydrogen immersion exposure of FRP pipelines and performed post-immersion qualification testing. Evaluations showed no evidence of hydrogen-induced degradation of the materials or pipeline performance.
 - Completed pipeline leakage measurements in Fiberspar FRP pipelines. The measured hydrogen leak rate of 0.02% per day is significantly smaller than that predicted using permeation coefficient measurements in liner material.
- Installed a new apparatus for measuring hydrogen diffusion and permeation coefficients in pipeline polymers.

Technical Barriers

The project addresses the following technical barriers from the Hydrogen Delivery section (3.2.4.2) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (D) High Capital Cost and Hydrogen Embrittlement of Pipelines

Introduction

Pipelines could be a feasible long-term solution for delivering large quantities of gaseous hydrogen over long distances and distributing it in urban and rural settings. However, there are hydrogen compatibility issues in steel pipelines, and the capital costs for pipeline installation must be dramatically reduced. Composite pipeline technology is a promising alternative to low-alloy high-strength steel pipelines from both performance and cost considerations. For instance, FRP pipelines are engineered composite pipelines that are widely used in upstream oil and gas operations and

in well interventions. FRP pipelines typically consist of an inner non-permeable liner that transports the fluid (pressurized gas or liquid), a protective layer applied to the liner, an interface layer between the protective layer and the reinforcement layers, multiple glass or carbon fiber reinforcement layers, an outer pressure barrier layer, and an outer protective layer. The pipeline has large burst and collapse pressure ratings, high tensile and compression strengths, and tolerates large longitudinal and hoop strains. Thousands of feet of continuous pipe can be unspooled and trenched as a seamless entity, and adjoining segments of pipeline can be joined in the trench without welding using simple connection techniques. The emplacement requirements for FRP pipelines are dramatically less than those for metal pipe; installation can be done in narrower trenches using light-duty, earth-moving equipment. This enables the pipe to be installed in areas where right-of-way restrictions are severe. In addition, FRP pipe can be manufactured with fiber optics, electrical signal wires, power cables or capillary tubes integrated within its layered construction. Sensors embedded in the pipeline can be powered from remote locations and real-time data from the sensors can be returned through fiber optics or wires. This allows the pipeline to be operated as a smart structure, providing the unique advantage of lifetime performance and health monitoring.

Approach

The challenges for adapting FRP pipeline technology to hydrogen service consist of evaluating the constituent materials and composite construction for hydrogen compatibility, identifying the advantages and challenges of the various manufacturing methods, identifying polymeric liners with acceptably low hydrogen permeability, critiquing options for pipeline joining technologies, ascertaining the necessary modifications to existing codes and standards to validate the safe and reliable implementation of the pipeline, and determining requirements for structural health monitoring and embedded real-time measurements of gas temperature, pressure, flow rate, and pipeline permeation.

These challenges are being addressed by performing bench-scale tests of FRP pipelines and constituent materials to determine their long-time compatibility with hydrogen, identifying pipeline liner materials that exhibit good performance in hydrogen environments, evaluating current methods for pipeline joining with consideration of the unique requirements for hydrogen service, and assessing the state-of-the-art in integrated sensing technologies for composite structures.

Results

We have been using a straightforward accelerated aging process to screen for hydrogen-induced damage

in FRP pipelines (Fiberspar LinePipe™) and pipeline constituent materials. The process involves immersion of FRP pipeline specimens in high-pressure (69 bar) hydrogen at an elevated temperature (60°C) to promote an accelerated interaction of hydrogen with the pipeline structure. To assess specific effects on the constituent materials in the pipeline, specimens of fiberglass rovings, resin matrix and liner materials were immersed simultaneously with the pipeline specimens, and all specimens were subjected to either a 1-month exposure (reported in the previous year) or an eight-month exposure (current year) to this hydrogen environment. At the conclusion of the exposure interval, the pipeline specimens were evaluated by Fiberspar for degradation using hydrostatic burst pressure tests to assess the overall integrity of the structure, compression tests to assess the integrity of the polymer matrix, and bend testing to assess the integrity of the laminate. The results of these tests were compared to the results obtained from identical tests performed on un-conditioned specimens from the same manufacturing run. Tensile tests and dynamic mechanical analysis were performed at ORNL on multiple specimens of constituent materials. The results of the specimens conditioned in hydrogen were compared to specimens that were conditioned in ambient-air for identical intervals.

Our results from the eight-month exposure were largely consistent with those from the one-month exposure; *there were no statistically significant differences between the test results of off-the-shelf and hydrogen-aged pipeline specimens and materials.* We found a small difference, however, between the tensile strengths of 1-month conditioned and 8-month conditioned glass fibers. Although statistically significant, these results are not conclusive. Thus we are in the process of repeating the hydrogen conditioning and accelerated aging on a larger number of glass fibers, performing more tensile tests at shorter intervals, and using statistical analysis that reduces the large error bars due to extreme values in the data sets.

We completed our measurements of the hydrogen leak rate in short sections of FRP pipeline. These measurements were designed to assess how well the pipeline contains high-pressure hydrogen gas. The measurements were done on off-the-shelf 10-cm inside diameter specimens of Fiberspar LinePipe™. The pipeline liner was 0.526-cm-thick pipeline grade high density polyethylene (PE-3408). The hydrogen pressurization in the pipelines was 103 bar (1,500 psia), which is the pipeline pressure rating, and all measurements were done at ambient lab temperatures. The pipeline was closed on each end using capped Fiberspar LinePipe™ connectors with elastomer (O-ring) seals. The leak rate was calculated from the temperature-corrected pressure decay curve. Changes in pipeline volume that occurred due to pressure-induced dimensional changes in the pipeline length and

circumference were measured using strain gauge sensors. These volumetric changes occurred at the earliest measurement times and diminished to near zero at the long measurement times during which the steady-state leak rate was determined.

To predict the hydrogen leak rate per meter of liner we used the expression

$$\frac{dn}{dt} = \frac{2\pi P}{\ln(b/a)}(p_0 - p_1) \quad \text{mol/s} \cdot \text{m}$$

where n is moles of hydrogen, P is the permeation coefficient for hydrogen in PE-3408, $a=5.05$ cm and $b=5.576$ cm are the inner and outer radii of the liner tube, and $p_0=100$ bar and $p_1=1$ bar are the hydrogen pressures inside and outside the liner. Our measurement of the permeation coefficient for PE-3408 found that $P \approx 4 \times 10^{-10}$ mol/m·s·bar. Thus the predicted leak rate for a 2.7-meter long pipeline specimen is -2.4×10^{-2} mol H_2 /h, assuming the leakage through the seals on the steel end caps seals is negligible compared to the leakage through the polymer liner.

Figure 1 shows the results of a long-term measurement of the hydrogen gas leak rate dn/dt in a 2.7-meter-long pipeline. During the first 500 hours the apparent leak rate steadily decreased. We attribute this apparent leak rate, which is larger than the constant leak rate observed after 500 hours, to two phenomena. First, the pipeline volume initially increased slightly as the composite structure slowly expanded under the stress of pressurization. This volumetric expansion produced a slight reduction in pressure and yielded an apparent reduction the number of moles of gas. Second, the pipeline wall (liner and reinforcement layers) absorbed

and retained hydrogen after it was pressurized. This also yielded an apparent decrease in the number of moles of gas. In the interval from 500 to 6,400 hours (20 to 270 days) the leak rate dn/dt was constant, and a linear least-squares fit to the leak rate in this interval gave a value of -5.4×10^{-4} mol H_2 /h. This leak rate is equivalent to a stored hydrogen loss of about 0.02% H_2 per day at a pressurization of 100 bar.

Table 1 shows the results of leak rate measurements of three lengths of pipeline. The three pipelines were identical with the exception of their lengths. The same pair of connector end caps was used on all specimens. In all three lengths the measured leak rate was significantly lower than the predicted rate. The leak rate should have increased in direct correspondence to the pipeline length, but for the two shorter lengths we probably terminated the measurement before the leak rate decreased to its steady-state (actual) value. (The pipeline wall might not yet have been saturated with hydrogen.)

TABLE 1. Results of hydrogen leak rate measurements in three Fiberspar LinePipe™ FRP pipeline specimens. All pipelines were identical with the exception of their lengths. The same pair of capped connectors was used on all specimens. The measurement intervals on the two shorter lengths were probably too brief to obtain a constant leakage rate, i.e., the pipeline wall was still being saturated with hydrogen, producing a virtual leak.

Pipeline Length m (ft)	Nominal Pressure bar (psia)	Measurement Duration h	Measured Leakage Rate mol/h	Predicted Leakage Rate mol/h
0.9 (3)	100 (1,500)	145	-4.4×10^{-4}	-8.1×10^{-3}
1.8 (6)	100 (1,500)	285	-5.5×10^{-4}	-1.6×10^{-2}
2.7 (9)	100 (1,500)	6,400	-5.4×10^{-4}	-2.4×10^{-2}

FIGURE 1. The leakage measured in a 2.7-m (9-ft) long specimen of 10-cm inside diameter Fiberspar LinePipe™ FRP pipeline with 0.5-cm thick high-density polyethylene liner, pressurized to approximately 100 bar (1,500 psia), was found to have a long-term (~6,400 hours observation) steady-state leak rate of 5.4×10^{-4} moles H_2 per hour leakage rate. This leakage rate is equivalent to a loss of 0.02% per day of hydrogen, a value substantially below the provisional 0.5% leakage goal.

We built a new, improved apparatus for measuring diffusion and permeation coefficients in pipeline polymers. This apparatus is being used to assess the efficacy of surface treatments on polymer specimens. We expect to be able to provide results of these measurements by the end of the project year.

We began the next step in hydrogen compatibility testing: evaluating composite pipelines for environment- and strain-induced hydrogen deterioration. The stress-related embrittlement behavior of pipeline steels in hydrogen environments is well known; it is therefore important to verify that the combinations of hydrogen environment-and-stress do not adversely affect composite pipeline integrity and service life. The evaluations we will perform are long-term stress rupture tests and high-pressure cyclic fatigue tests. The stress rupture tests measure time-to-rupture under constant hydrogen pressure. Stress rupture testing is the American Petroleum Institute (API) basis for qualifying the pressure rating of the pipe body [2]. High-pressure

cyclic fatigue tests provide information on pipeline integrity after repeated hydrogen gas pressurization-depressurization cycles. The fatigue tests will provide information that can't be derived from constant pressure testing, including liner collapse resistance (similar to blowdown testing), resistance to micro-cracking, crazing, crack propagation, fiber-resin interface failure, etc. of composite reinforcement layer, resistance to environmental stress-corrosion phenomena, and an assessment of the integrity of joint attachment/joint sealing under cyclic loading. We expect to publish results of these tests in the next project year.

Conclusions and Future Directions

- No observed hydrogen incompatibility in composite pipeline materials after accelerated aging testing.
- Hydrogen leakage rates in off-the-shelf FRP pipelines are much better than expected, and a strong argument can be made that they are significantly lower than the leakage target.
- We expect to begin the next phase of hydrogen compatibility testing by evaluating composite pipelines for environment- and strain-induced hydrogen deterioration.
 - Objective: Verify that the combinations of hydrogen environment-and-stress do not adversely affect composite pipeline integrity and service life.
- Perform long-term stress rupture tests and high-pressure cyclic fatigue tests.
 - Stress rupture testing is the API prescription for qualifying the pressure rating of the pipeline.
 - High-pressure cyclic fatigue tests provide information on pipeline integrity after repeated hydrogen gas pressurization-depressurization cycles.
 - Fatigue tests provide information that can't be derived from constant pressure testing, including liner collapse resistance (similar to blowdown testing), resistance to micro-cracking, crazing, crack propagation, fiber-resin interface failure of composite reinforcement layer, resistance to environmental stress-corrosion phenomena.
- Subject pipeline specimens to 4-pt flexural bending to produce microcracks before leak rate measurements to reveal the extent that microcracking increases permeation and leakage.
- Measure hydrogen pressure inside pipeline wall as a function of depth in wall and within composite layers to determine hydrogen concentration gradient in the wall.
- Assess the integrity of joint attachment/joint sealing under cyclic loading.
- Out-year plans: Evaluate feasibility of large-scale manufacturing operations, plan prototype manufacturing for a demonstration project, manufacture prototype FRP pipeline for hydrogen service, coordinate commercial demonstration of pipeline technology.

FY 2009 Publications/Presentations

1. 2009 DOE Hydrogen Program Annual Merit Review – Arlington, Virginia – May 19, 2009, Presentation PDP24.

References

1. HFCIT MYRDD Plan, Table 3.2.2, page 3.2-13, and footnote b, page 3.2-16.
2. *Qualification of Spoolable Reinforced Plastic Line Pipe*, API Recommended Practice 15S, First Edition, March 2006.

III.17 FY 2009 SRNL Hydrogen Delivery Project—Hydrogen Permeability and Pipeline Integrity/Fiber Reinforced Composite Pipeline

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Project Start Date: October 1, 2006
Project End Date: October 1, 2012

- Pipeline Transmission and Distribution Cost: \$0.6 M/mile and \$0.27 M/mile, respectively
- Hydrogen Leakage: TBD--<0.5% by 2017

Accomplishments

- Completed 9-month hydrogen exposures for FRP pipe sections, compression samples, tensile and dynamic mechanical analysis (DMA) samples.
- Completed commercial FRP joint leakage testing—established leak testing protocols and defined relevant testing conditions.
- Initiated FRP flexural load leak testing.
- Initiated FRP cyclic load leak testing.

Objectives

Fiber Reinforced Composite (FRP) Pipeline

- Focused evaluation of FRP piping for hydrogen service applications.
- Assessment of the structural integrity of the FRP piping and leakage of existing commercial available FRP joint designs and joint components.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Delivery section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (D) High Capital Cost and Hydrogen Embrittlement of Pipelines
- (I) Hydrogen Leakage and Sensors
- (K) Safety, Codes and Standards, Permitting

Technical Targets

This project is focused on the evaluation of FRP piping for hydrogen service applications. Assessment of the structural integrity of the FRP piping and the individual manufacturing components in hydrogen will be performed. Insights gained will support qualifications of these materials for hydrogen service including the DOE 2012 delivery targets:

Introduction

The use of FRP materials for hydrogen service will rely on the demonstrated compatibility of these materials for pipeline service environments and operating conditions. The ability of the polymer piping to withstand degradation while in service, the fiber strength wrapping to resist hydrogen attack, and the fiber-resin interface to remain intact are all critical to the successful implementation of these materials for hydrogen pipeline. The goal of the overall project is to successfully adapt spoolable FRP from oil and natural gas use to high-pressure hydrogen use. As such, the current research effort has been focused on two aspects: 1) long-term exposures of FRP piping sections and materials to gaseous hydrogen for subsequent materials property testing, and 2) evaluation of leakage behavior of existing commercially available FRP joints and joint components.

Approach

SRNL has performed environmental exposure testing under accelerated conditions to simulate aging effects on FRP piping materials. This testing involves exposures of short piping sections to pure hydrogen environments at both ambient and non-ambient temperatures (140°F) and pressures of approximately 1,000 psig in order to evaluate hydrogen compatibility.

Additionally, a testing program has been initiated to evaluate current existing metallic joint components for FRP piping. Commercially available joint types are being leak tested and leakage rates recorded. The leak rate data for the joints will be applied to determine the

acceptability of existing metal joints available for FRP pipe and will also aid in the development of new joint materials and designs if necessary for hydrogen service.

Results

Testing of FRP materials in Fiscal Year 2008 has focused on two major areas: 1) environmental exposure of FRP pipe section and materials of construction to gaseous hydrogen, and 2) leak testing of commercial FRP joint components. SRNL has completed the 9-month environmental exposures in support of Oak Ridge National Laboratory's (ORNL's) FRP materials testing effort. Multiple 4-ft sections of 2.5" outside diameter (OD) FRP pipe and materials test samples—tensile dog-bones, compression rings, DMA test strips—have been exposed to 99.9995% hydrogen gas at nominally 140°F and 1,000 psig in the newly designed, fabricated, and installed SRNL FRP hydrogen exposure station. Following exposure of these materials to gaseous hydrogen ORNL will work with a commercial FRP vendor to subject the 4-ft pipe sections to commercial standard product quality tests in addition to internally conducting materials evaluation testing on the exposed test samples.

In addition to the hydrogen exposure testing, leakage testing of commercially available FRP joint components has been initiated. Samples of 2.5" OD FRP piping with attached end fittings and joint fittings from two major FRP piping vendors—Fiberspar and Polyflow—have been procured. The Fiberspar technology makes use of an O-ring compression mechanical system to maintain seal integrity while the Polyflow uses a high pressure hydraulically crimped technology.

Leak tests for these typical joint/end-fitting components were conducted using two approaches. The first approach used conventional helium detection technology with a leak sensitivity of 1×10^{-9} cc/sec. Results from the helium leak rate determination for the Fiberspar O-ring compression system and the Polyflow hydraulically crimped system are as follows: 1) Fiberspar--> 1×10^{-4} stdcc/sec @ 1 atm and room temperature and 2) Polyflow--> 1×10^{-5} stdcc/sec @ 1 atm and room temperature. Evaluation of these He leak rate values was higher than expected, however, from previous research effort it was known that He leakage rates can be higher than actual hydrogen leak rates due to the He molecule being smaller than the diatomic hydrogen molecule.

As a result, pressure decay testing using gaseous hydrogen at 1,000 psig was initiated for both joint/end-fitting designs. Results from this testing have indicated leak rates on the order of $> 1 \times 10^{-2}$ stdcc/sec for 1-hr durations. Additional testing of the FRP pipe materials under flexural load to simulate trench earth movement has also been conducted. Leakage rates from these test indicate only minor increases in leakage for test conducted at a 2" deflection (Figure 1).

FIGURE 1. Flexural Load Leakage Testing of FRP Piping

Finally, in order to evaluate the stability of the hydraulically crimped end fitting for one of the FRP manufacturers tested as part of this project, cyclic load leak testing was conducted. The cyclic load leak testing consisted of subjecting a 4-ft section of FRP piping with hydraulically crimped end fittings to 100 cycles of pressure load from 0-1,000 psig followed by pressure decay leak testing previously described. Results from this cyclic loading showed no indication of increased leakage for the hydraulically crimped end-fittings after 100 pressure cycles.

Conclusions and Future Directions

Conclusions

- Critical issue for demonstrating the feasibility of FRP pipeline for hydrogen service is development of the technical basis to demonstrate structural integrity by defining FRP susceptibility to hydrogen embrittlement.
- Qualification of existing commercial FRP joint components with respect to leakage identified in the Department of Transportation gap analysis report as one of four major needs for demonstrating composite FRP piping feasibility.
- Leakage results indicate acceptable leak rates for FRP joint fittings.
- Initial leakage rates for FRP flexural load testing indicate minor increase in leakage rate under flexural load for a 2" deflection.
- Cyclic load testing of crimped FRP end fittings indicate no increase in leakage rate.

Future Work

- Initiate FRP life management methodology development.
- Initiate flaw tolerance/third party damage testing for FRP.
- Evaluation of environmental degradation of FRP.

FY 2009 Publications/Presentations

1. SRNL FRP Piping Project, Presentation to Hydrogen Delivery Pipeline Working Group, Sandia National Laboratory, February 21, 2008.
2. SRNL FRP Piping Project, Presentation to Hydrogen Delivery Pipeline Working Group, Jackson Hole, WY–Post Hydrogen Effects Conference, September 5, 2008.

III.18 Materials Solutions for Hydrogen Delivery in Pipelines

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Contract Number: DE-FG36-05-GO 15036

Subcontractors:

- Evraz North America (formally Oregon Steel Mills), Portland, OR
- Schott North America, Duryea, PA
- Chemical Composite Coatings Int'l, LLC, Alpharetta, GA
- Advanced Technology Corporation (ATC), Oak Ridge, TN
- Columbia Gas of Kentucky, Lexington, KY
- ASME Standards Technology LLC, New York, NY
- DGS Metallurgical Solutions, Inc, Vancouver, WA
- Hatch Mott MacDonald, Monroe, LA
- Reference Metals Company, Bridgeville, PA

Start Date: May 2005

Projected End Date: September 2010

Objectives

Overall goal of the project is to develop materials technologies that would enable minimizing the problem of hydrogen embrittlement associated with the high-pressure transport of hydrogen.

- Identify steel compositions and processes suitable for construction of a new pipeline infrastructure or potential use of the existing steel pipeline infrastructure.
- Develop barrier coatings for minimizing hydrogen permeation in pipelines and associated processes.
- Understand the economics of implementing new technologies.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Delivery section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (D) High Capital Cost and Hydrogen Embrittlement of Pipelines
- (K) Safety, Codes and Standards, Permitting

Technical Targets

The objective of the project is to develop materials technologies that would enable minimizing the problem of hydrogen embrittlement associated with the high-pressure transport of hydrogen through pipelines. Such materials technologies in combination with cost-effective excavation and fabrication technologies will facilitate reducing the capital cost of pipelines. Insights gained from these studies will be applied toward the design and construction of hydrogen delivery systems that meet the following DOE 2012 hydrogen delivery pipeline transmission targets:

- Reliability (relative to hydrogen embrittlement concerns and integrity):
 - Evaluate hydrogen embrittlement characteristics of existing commercial pipeline steels under high-pressure hydrogen.
 - Evaluate hydrogen embrittlement characteristics of existing alternative commercially available steels under high-pressure hydrogen.
 - Develop alternate alloys and evaluate hydrogen embrittlement.
 - Develop coatings to minimize dissolution and penetration of hydrogen and evaluate hydrogen embrittlement in coated alloys.
- Pipeline Transmission Total Capital Cost (\$/Mile): \$0.60 for 16" outside diameter (OD) transmission pipeline.
 - Financial analysis and incorporation into codes and standards.

Accomplishments

Accomplishments to date are as follows:

- Four commercially available pipeline steels along with two commercially available alternative steels have been down-selected for initial study of their hydrogen embrittlement characteristics under high pressure hydrogen.

- Majority of the baseline pipeline steel microstructure and mechanical property data have been characterized.
- Commercial X70 pipeline welds available.
- Two traditional screening tests have been explored.
- In situ automated ball indentation test has been developed.
- Processing techniques developed for glassy coatings, down-selected composition has been coated for properties and microstructural analyses.
- In situ tensile testing at Oak Ridge National Laboratory (ORNL) complete:
 - Two strain rates - 1×10^{-4} , 1×10^{-5}
 - Hydrogen vs. helium
 - Three pressures – 800 psi, 1,600 psi, 3,000 psi
 - Total initial tests = 48, additional validation testing = 10, additional statistical testing of alloy A and B
- Actual construction costs of a pipeline project supplied by Columbia Gas of Kentucky reviewed by the project team.
- Note that all work related to coatings has been placed on hold per DOE.

Introduction

Pipeline transmission is the most economical method for hydrogen delivery in large quantities from the point of generation to point of use. As transmission pressures are increased, steel pipelines that could be used for the transport of hydrogen at low pressures are prone to hydrogen embrittlement at the welds, the heat-affected-zone and/or the base metal regions in the pipeline. Over the past few years, significant advances have been made in understanding the mechanisms of hydrogen embrittlement in a wide variety of materials and in materials technologies. The increasing integration of computational techniques with experimental methods has resulted in the development of “designer” materials along with the scientific methodologies for developing customized materials better suited for any given application. New coating materials and coating technologies hold promise in developing barrier coatings to minimize the dissolution and permeation of hydrogen through steels.

The work on this project represents an integrated approach to developing and testing new materials solutions to enable pipeline delivery of hydrogen at high pressures. The scope of the project includes (1) identification of steel compositions and associated welding filler wires and processes that would be suitable for new pipeline infrastructure or indicate use of existing pipeline infrastructure for transport of

hydrogen at requisite high pressures, (2) development of barrier thin film coatings that would minimize the hydrogen permeation in the current natural gas pipelines and (3) understanding the cost factors related to the construction of new pipelines and modification of existing pipelines and to identify the path to cost reduction. The team participating in this proposal is lead by Secat, Inc. and includes ORNL, DGS Metallurgical Solutions, Inc., ASME Standards Technology, LLC, University of Illinois, Schott North America-Regional R&D, Columbia Gas, Chemical Composite Coatings International LLC, Advanced Technology Corporation, Evraz North America (formerly Oregon Steel Mills), Reference Metals Company and Hatch Moss MacDonald.

Approach

Achievement of an understanding to the mechanisms of hydrogen embrittlement of commercially available transmission pipeline steels and welding consumables will involve characterization of the mechanical properties and microstructures in both the absence and presence of high pressure hydrogen gas. The study of vintage pipeline steels along with current pipeline steel technology and potential alternative alloy designs will help determine the optimum mechanical properties and microstructure required to operate in a high pressure hydrogen gas environment. Both in situ and ex situ methods will be used to study the effect of hydrogen gas under pressure on microstructural and mechanical properties. Thermokinetic modeling and microstructural characterizations will be used in the analysis.

In addition, glass and oxide coatings to impede the permeation of hydrogen gas to the steel will be explored, developed and tested in the presence of high pressure hydrogen gas. Coated steel mechanical properties in the presence of high pressure hydrogen gas will be tested and compared to uncoated specimens. Successful coatings will be tested for resistance to damage related to required pipeline operational non-destructive testing techniques.

Factors related to materials and construction costs are incorporated into the project. This understanding will allow for recommendations for optimum material selections and fabrication of transmission pipeline systems suitable for high pressure hydrogen gas transport.

Results

Four commercially available pipeline steels and two commercially available alternative steels have been down-selected for initial study of their hydrogen embrittlement under high pressure hydrogen. The compositions of these steels are shown in Table 1.

It is anticipated that a study of these steels would be representative of advanced steels and would point to additional compositions that need to be studied in order to develop an appropriate relationship between compositions, structure, and hydrogen embrittlement characteristics.

Mechanical properties, microstructural characterizations, thermokinetic modeling, ex situ high pressure hydrogen testing, ATC 2,000 psi testing, and corrosive National Association of Corrosion Engineers (NACE) testing of the four pipeline alloys have been completed. All of these results have been reported prior. All of this testing has shown that microstructural differences cause different behaviors in the presence of hydrogen. Some of the behaviors appear to be positive while others may appear negative.

Glass coating development has been progressing and has been reported in previous reports. In addition, actual costs to construct a natural gas pipeline were

supplied by Columbia Gas of Kentucky. These costs were reviewed, discussed and reported in previous reports. Changing economic conditions will affect the cost of steel and will require review of these construction costs in the future.

ORNL has completed the tensile testing matrix at three different pressures (800, 1,600, 3,000 psi) and two different strain rates (10^{-4} , 10^{-5}) for the four commercially selected pipeline steels (alloys A-D) in Table 1. Reduction in area was measured for each pressure/ alloy. All four of the alloy designs had an initial drop in reduction in area at 800 psi hydrogen for each strain rate. However, the drop in reduction in area varied by alloy design (i.e. – microstructure) and with increasing pressure each alloy design performed differently. From this testing the ferrite/acicular ferrite microstructure design of alloys B and D performed the best across the pressure range (Figures 1 and 2). In addition, ORNL performed statistical tensile testing of alloys A and B

TABLE 1. Compositions of Steels Selected for Initial Study of Hydrogen Embrittlement under High Pressure Hydrogen (all in wt%)

	Grade	C	Mn	Si	Cu	Ni	V	Nb	Al	Cr	Ti
A	API X70	0.08	1.53	0.28	0.01	0	0.05	0.061	0.031	0.01	0.014
B	API X70/ X80	0.05	1.52	0.12	0.23	0.14	0.001	0.092	0.036	0.25	0.012
C	API X70/ X80	0.04	1.61	0.14	0.22	0.12	0.0	0.096	0.037	0.42	0.015
D	API X52/ X60	0.03	1.14	0.18	0.24	0.14	0.001	0.084	0.034	0.16	0.014
E*	100 KSI Yield Structural	0.08	1.71	0.22	0.06	0.67	0.002	0.044	0.039	0.01	0.038
F*	400 BHN Abrasion Resistant	0.15	1.42	0.42	0.05	0.02	0.003	0.014	0.038	0.22	0.035

*Alloy E and F contain 0.0017 and 0.0023 boron, respectively. Alloy F contains molybdenum of 0.32.

FIGURE 1. In Situ High Pressure Gaseous Hydrogen Tensile Test Results (Reduction in Area) at 10^{-4} Strain Rate from ORNL of Alloys A-D

FIGURE 2. In Situ High Pressure Gaseous Hydrogen Tensile Test Results (Reduction in Area) at 10^{-5} Strain Rate from ORNL of Alloys A-D

which in both cases showed no effect on actual yield and ultimate strengths at the three pressure ranges. Fracture stress was the only variable affected in the presence of hydrogen gas (Figures 3 and 4).

From this work, alloys B and D were chosen for additional fracture and fatigue testing for full mechanical property characterization at 800 and 3,000 psi.

Remaining work for Fiscal Year 2009 includes:

- Validation testing of initial ORNL tensile testing of selected data points.
- Transmission electron microscopy microstructural characterization of bainitic structures of alloys A–D.

FIGURE 3. In situ High Pressure Gaseous Hydrogen Statistical Tensile Test Results (Reduction in Area) at 10^{-5} Strain Rate from ORNL of Alloys A and B

FIGURE 4. In situ High Pressure Gaseous Hydrogen Statistical Tensile Test Results (Strength) at 10^{-5} Strain Rate from ORNL of Alloy B

- Fracture and fatigue testing of alloys B and D at 800 and 3,000 psi.

Conclusions and Future Directions

Preliminary testing in FY 2006, FY 2007 and FY 2008 showed that high pressure hydrogen may have an effect on mechanical properties depending on microstructure design. Additional limited testing at ATC showed that mechanical properties, especially fracture toughness can be affected in the presence of high pressure hydrogen. NACE testing demonstrated that microstructure; especially those containing pearlite are susceptible to cracking in the presence of hydrogen. ORNL high pressure in situ tensile testing has been completed at three different pressures and two strain rates. Using reduction in area as the comparison criteria, two alloys (B and D) had the best performance across the pressure range. This supports that microstructure is a critical component of resistance to hydrogen embrittlement and needs to be fully understood. Alloys B and D were selected for additional fracture and fatigue mechanical testing to complete the mechanical property characterization in the presence of high pressure (800 and 3,000 psi) gaseous hydrogen.

Pending future funding in FY 2010, the following represents additional work:

Steels

- In situ tensile testing of down selected alternative alloy/microstructure (alloy E and F) designs at three pressures (800, 1,600, 3,000 psi) and strain rates (10^{-4} , 10^{-5}).
- Fracture and fatigue testing of best performer of alloys E and F at 800 and 3,000 psi.
- Characterize the effect of one impurity gas on properties evaluated using in situ tensile testing.
- Volume fractions of microstructure thresholds, pressure thresholds, other factors (industrial surface oxide, etc.).
- Complete microstructural characterization of down-selected steels after exposure to hydrogen to understand the effect of microstructure on embrittlement.
- Add alloys with higher volume fraction of pearlite (~10-30%, represents older 1950-1980's pipeline metallurgy) or various volume fractions of bainite or different types of bainite to the in situ testing to evaluate volume fraction thresholds.
- Complete thermodynamic and kinetic modeling of initial down-selected alloys D-F composition.
- Pipeline weld sample microstructural and hydrogen pressure and time can be included in the testing.
- Additional information gathered will be shared with the ASME B31.12 Hydrogen Piping and Pipelines

codes and standard committee for review and consideration for incorporation. This will be done through partners ASME and DGS Metallurgical Solutions.

Economic Analysis

- Recommend steel and coating systems for implementation.
- Evaluate economic impact of suggested materials systems.

Results from the testing will be used to help identify optimum alloy/microstructure design required to safely transport high pressure hydrogen gas through steel pipelines. Some of these alloy/microstructure designs may already exist in the existing pipeline infrastructure.

FY 2009 Publications/Presentations

1. An oral presentation regarding the overall project status was given at the DOE Pipeline Working Group Meeting – Jackson Hole, WY (September 2008).
2. An oral presentation regarding the overall project status was given at the DOE Annual Merit Review Meeting (May 2009).
3. G. Muralidharan, J.P. Strizak, N.D. Evans, D.G. Stalheim, and S.K. Das, “Effect of Microstructure on Hydrogen Embrittlement of Pipeline Steels”, Hydrogen08 Conference, Jackson Hole, WY USA, 2008.
4. D. Stalheim, L. Hayden, “Metallurgical Considerations for Commercial Steels used for Hydrogen Service”, Hydrogen08 Conference, Jackson Hole, WY USA, 2008.

References

1. “Materials Solutions for Hydrogen Delivery” in Pipelines 2008 Oral Presentation from the DOE Pipeline Working Group Meeting, Jackson Hole, WY (September 2008).
2. “Materials Solutions for Hydrogen Delivery” in Pipelines 2009 Oral Presentation from the DOE Annual Merit Review Meeting (May 2009).

III.19 Hydrogen Embrittlement of Pipelines: Fundamentals, Experiments, Modeling

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Objectives

- Mechanistic understanding of hydrogen embrittlement in pipeline steels in order to devise fracture criteria for safe and reliable pipeline operation under hydrogen pressures of at least 15 MPa and loading conditions both static and cyclic.
- Explore methods of mitigation of hydrogen-induced failures through inhibiting species (e.g., water vapor) or regenerative coatings (e.g., surface oxidation).
- Explore suitable steel microstructures to provide safe and reliable hydrogen transport at reduced capital cost.
- Assess hydrogen compatibility of the existing natural gas pipeline system for transporting hydrogen.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Delivery section of the DOE Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan (HFCIT Multi-Year RD&D Plan):

- (D) High Capital Cost and Hydrogen Embrittlement of Pipelines
- (G) Storage Tank Materials and Costs
- (K) Safety, Codes and Standards, Permitting

Technical Targets

This project is conducting fundamental studies of hydrogen embrittlement of materials using both numerical simulations and experimental observations of the degradation mechanisms. Based on the understanding of the degradation mechanisms the project's goal is to assess the reliability of the existing natural gas pipeline infrastructure when used for hydrogen transport, suggest possible new hydrogen-compatible material microstructures for hydrogen delivery, and propose technologies (e.g. regenerative coatings) to remediate hydrogen-induced degradation. These studies meet the following DOE technical Targets for Hydrogen Delivery as mentioned in Table 3.2.2 of the HFCIT Multi-Year RD&D Plan:

- *Pipelines: Transmission*—Total capital investment will be optimized through pipeline engineering design that avoids conservatism. This requires the development of failure criteria to address the hydrogen effect on material degradation (2012 target).
- *Pipelines: Distribution*—Same cost optimization as above (2012 target).
- *Pipelines: Transmission and Distribution*—Reliability relative to H₂ embrittlement concerns and integrity, third party damage, or other issues causing cracks or failures. The project's goal is to develop fracture criteria with predictive capabilities against hydrogen-induced degradation (2017 target). It is emphasized that hydrogen pipelines currently in service operate in the absence of design criteria against hydrogen-induced failure.
- *Off-Board Gaseous Hydrogen Storage Tanks (Tank cost and volumetric capacity)*—Same cost optimization as in *Pipelines: Transmission* above. Current pressure vessel design criteria are overly conservative by applying conservative safety factors on the applied stress to address subcritical cracking. Design criteria addressing the hydrogen effect on material safety and reliability will allow for higher storage pressures to be considered (2010 target).

Accomplishments

- Began using focused ion beam (FIB) machining to lift-out sections from fracture surfaces along with transmission electron microscopy (TEM) analysis of the extracted thin foils to reveal the nature and identify the characteristic details of the degradation mechanisms.

- Characterized the microstructure of pipeline steels through optical analysis, scanning electron microscopy (SEM), and TEM, and identified particle composition through energy dispersive spectroscopy for: a) laboratory specimens from Air Liquide, Air Products, and Kinder-Morgan industrial pipelines; b) new microalloyed, low-carbon steels from Oregon Steel Mills (OSM) provided by DGS Metallurgical Solutions, Inc.
- Measured the macroscopic flow characteristics of the new microalloyed, low-carbon steels, possibly hydrogen compatible.
- Determined the hydrogen permeability of steels from OSM and Kinder-Morgan.
- Developed a thermodynamic theory of hydrogen-induced decohesion that was used to model and simulate hydrogen-induced subcritical cracking.
- Developed modeling and simulation capabilities of transient hydrogen transport accounting for the mechanical deformation of the pipeline microstructure. Predictions have been made of a) fracture initiation through void nucleation at inclusions, and b) threshold stress intensities associated with subcritical crack growth.
- Determined the intensity of the hydrostatic constraint ahead of an axial crack on the inside surface. Laboratory specimen type (hydrostatic constraint guidelines) has been identified to investigate fracture processes in a real-life pipeline.

Introduction

Hydrogen is a ubiquitous element that enters materials from many different sources. It almost always has a deleterious effect on material properties. The goal of the project is to develop and verify a lifetime prediction methodology for failure of materials used in pipeline systems and welds exposed to high-pressure gaseous environments. Development and validation of such predictive capability and strategies to avoid material degradation is of paramount importance to the rapid assessment of the suitability of using the current pipeline distribution system for hydrogen transport and of the susceptibility of new alloys tailored for use in hydrogen related applications.

Through our hydrogen permeation rig, we measured the permeability of steel samples from industrial pipelines (Kinder-Morgan) and some new possibly hydrogen-compatible microalloyed, low-carbon steels provided by OSM. We used electron microscopy techniques to characterize the microstructure of these steels. Such characterization is important for the identification of the hydrogen trapping states in the material. We began using FIB machining to to

lift out sections from the fracture surfaces in order to understand whether hydrogen-induced fracture follows a cleavage plane or a slip plane. We carried out finite element calculations of transient hydrogen transport simulating hydrogen uptake and transport through an axial crack on the inside surface of a pipeline, and determined through constraint fracture mechanics that the single edge notch tension specimen is the appropriate laboratory specimen for the study of the fracture resistance of a pipeline. We studied the hydrogen effect on void nucleation at inclusions and calculated the hydrogen-induced reduction of the fracture toughness of pipeline steels containing MnS inclusions (natural gas pipeline steels). Further, we established the methodology to calculate threshold stress intensities for subcritical cracking which is of paramount importance to assessing whether a crack on the inside surface of a pipeline shall remain subcritical.

Approach

Our approach integrates mechanical property testing at the microscale, microstructural analyses and TEM observations of the deformation processes of materials at the micro- and nano-scale, first principle calculations of interfacial cohesion at the atomic scale, and finite element modeling and simulation at the micro- and macro-level.

In order to come up with fracture criteria for safe pipeline operation under hydrogen pressures of at least 15.0 MPa, we investigate the interaction of hydrogen transient transport kinetics with material elastoplastic deformation ahead of an axial crack either on the inside or the outside surface of a pipeline. Understanding of this interaction requires the determination of the elastic and flow characteristics of pipeline materials in the presence of hydrogen, and the measurement of the hydrogen adsorption, permeability, and bulk diffusion characteristics, such as the nature and strength of microstructural trapping sites for hydrogen. These experimental data are used in finite element simulations of the hydrogen distribution ahead of a crack tip in an effort to understand the transient and steady-state hydrogen population profiles. In addition, we use FIB machining to lift out sections from the fracture surfaces to explore and identify the nature of the hydrogen-induced fracture processes/events.

To quantitatively describe the hydrogen effect on internal material cohesion as a function of the hydrogen concentration under transient hydrogen conditions, we devised a thermodynamic theory of decohesion at internal material interfaces such as grain boundaries, precipitate/matrix, and second-phase/matrix interfaces. First-principles calculations of the hydrogen effect on these interfaces (see 2008 annual progress report), which constitute potential fracture initiation sites, are used to calibrate the parameters of the thermodynamic theory

such as the ratio of the reversible work of separation in the presence of hydrogen to that in the absence of hydrogen. The first-principles calculation results and the thermodynamics-based description of material cohesion provide hydrogen-dependent traction-separation laws. The combined information for the fracture mechanisms from the experiments and hydrogen concentration profiles from the simulations will help to establish the regime of critical hydrogen concentrations and critical elapsed time for a crack to remain stable under high hydrogen pressure. Quantitatively this will be assessed through the development of engineering fracture criteria in terms of macroscopic parameters.

Results

Identification and Characterization of the Fracture Mechanisms

Optical and SEM analyses show that hydrogen-induced fractures are distinctly different from the cold fast fractures in the compact tension specimens in the absence of hydrogen. In addition, the new microalloyed, low alloy carbon steels from the OSM exhibit fracture

surfaces which are not characteristic (see Figure 1 for D type steel; a typical low carbon [0.03% by wt] Mn-Si-single microalloy API/Grade X60, a predominantly ferrite microstructure with some pearlite) of the ductile mode of fracture expected for pipeline steels (existing natural gas pipelines).

To understand the fracture processes, we use TEM studies of samples taken from just below the fracture surface by the lift-out technique using FIB machining. The FIB lift-out technique is generally used on flat polished surfaces, but we have recently developed a means of lifting out samples directly from a rough fracture surface. Figure 1 shows the location of the top edge of the FIB sample with respect to the fracture surface. From the fracture surface of a compact tension specimen, trenches can be milled directly into the fracture surface and a thin membrane sampling perpendicular to the fracture surface can be lifted out, Figure 2.

Prior to the TEM examination, the lifted-out sample is thinned to electron transparency (Figure 2f). Microstructural features such as a grain boundaries and secondary phases such as carbides immediately below the fracture surface can be identified. Also,

FIGURE 1. Location of FIB lift-out sample from fracture surface of a compact tension specimen of D steel fractured in hydrogen at Sandia National Laboratories.

FIGURE 2. FIB lift out process: a) area of interest is located and a platinum strip is deposited; b) trenches are milled on either side of the platinum strip; c) a u-cut is made; d) micromanipulator is attached to the sample, and sample is cut free; e) sample is attached to a copper grid; f) sample is thinned to electron transparency.

evidence of plasticity such as dislocation structures immediately below the fracture surface can be observed and identified. The goal is to discover the nature of the fracture mechanisms of pipeline steels in a hydrogen environment.

Characterization and identification of the hydrogen/induced fracture processes/events is required for all objectives of the project.

Permeation Measurements and Microstructural Characterization

As described in previous annual progress reports, we continue using our permeation device to carry out permeation measurements for the D type steel provided by OSM – a typical low carbon (0.03% by wt) Mn-Si-single microralloy API/Grade X60, a predominantly ferrite microstructure with some pearlite. This alloy was found to perform very well in sour natural gas service. Microstructural characterization of this steel is also underway.

The design of the permeation experimental apparatus and the related hydrogen permeation measurements meet all objectives of the project.

Micro- and Macro-Modeling and Simulation

We used our hydrogen-transport/material-deformation simulation tool (see 2008 annual progress report) to carry out numerical simulations for the prediction of the macroscopic response of materials in the presence of hydrogen. In particular, we simulated the hydrogen effect on i) subcritical crack growth by intergranular failure. The calculated threshold stress intensity factor is a material parameter that can be used to design components against hydrogen-induced brittle fracture; ii) on void nucleation at inclusions followed by subsequent crack propagation. This scenario pertains to microstructures of medium/low strength steels used in the current natural gas pipelines; iii) issues of transferability between laboratory specimen fracture toughness results and real-life pipeline response. Highlights of all three simulation cases are as follows:

i) *Subcritical crack growth by grain boundary decohesion*: Conducting slow crack growth experiment with wedge opening load (WOL) specimens (Figure 3a) of alloy IN903, Moody *et al.* [1,2] observed that at hydrogen gas pressures larger than 45 MPa material cracks propagate intergranularly (Figures 3b,c). To simulate the mechanics of sustained-load cracking in a gaseous hydrogen environment, we used the thermodynamic theory of interfacial decohesion

FIGURE 3. Hydrogen-induced subcritical crack growth in alloy IN903: a) schematic of the WOL specimen used in the experiments; b) micrograph showing intergranular cracking at high hydrogen gas pressure; c) experimentally measured threshold stress intensity factor as a function of hydrogen concentration in the specimen in equilibrium with the hydrogen gas; d). simulation predictions of threshold stress intensity factor vs. time at various magnitudes of the interfacial diffusion coefficient. The parameters $\kappa = 0.138$ denotes the ratio of the cohesive energy of hydrogen-saturated grain boundary to the cohesive energy of the hydrogen-free grain boundary.

of Mishin *et al.* [3] to model intergranular crack propagation in alloy IN903.

According to Mishin *et al.* [3], the grain boundary cohesion is characterized by a traction-separation law phrased as

$$\sigma(c_{int}, q) = \frac{27}{4} \sigma_{max} [1 + (\kappa - 1)c_{int}/c_c] q(1 - q)^2, \quad (1)$$

where σ_{max} is the cohesive stress in the absence of hydrogen, c_{int} is the grain boundary hydrogen concentration in hydrogen atoms per metal atom, c_c is the concentration when the grain boundary is saturated, κ is the ratio of the cohesive energy of the saturated boundary to the cohesive energy of the hydrogen free boundary, and $q = \delta/\delta_c$ is non-dimensionalized separation with δ_c being the critical separation for complete failure of the grain boundary.

For the transient hydrogen transport problem, we assumed that hydrogen diffuses through the bulk

material [4] while it diffuses along the separating grain-boundary interface during crack propagation. Hydrogen transport along the grain-boundary interface is motivated by the gradient of the chemical potential μ_{int} of hydrogen which is given [3] by

$$\mu_{int} = N_A(\epsilon_B - \epsilon_A)/c_c + \frac{N_A(\phi_B^0 - \phi_A^0)}{c_c} [4(1 - q)^3 - 3(1 - q)^4] + R\Theta \ln \frac{c_{int}}{\beta_{int} - c_{int}}, \quad (2)$$

where N_A denotes Avogadro's number, ϵ_A and ϵ_B are respectively twice the surface energy of the material with no hydrogen and under saturation c_c , ϕ_A^0 and ϕ_B^0 are the cohesive energies of the grain boundary with no hydrogen and under saturation respectively in the absence of stress, β_{int} denotes the number of available sites for hydrogen occupancy per host atom on the grain boundary, $R = 8.314 \text{ J/mol K}$ is the universal gas constant, and Θ is the temperature.

The values of the parameters in Eq. (1) used in the calculations are reported in the work of Dadfarnia *et al.* [5]. In particular, the parameter κ was taken equal to 0.138 indicating a maximum cohesive energy reduction

by hydrogen of 86%. Such a reduction also accounts for the amount of plastic dissipation upon decohesion. The diffusion coefficient of hydrogen through the normal interstitial sites (NILS) of the bulk material surrounding the propagating crack was taken $D = 1.66 \times 10^{-15} \text{ m}^2/\text{s}$ [5] for room temperature at 295 K.

As hydrogen diffuses through the separating grain boundaries and the normal interstitial lattice sites (NILS) sites in the bulk material, there is a continuous exchange of hydrogen on the boundaries and in the adjacent grains such that continuity of the chemical potential of hydrogen is maintained. This provides the coupling between concurrent hydrogen transport through the matrix and along the grain boundaries. We solved the coupled bulk-diffusion/grain-boundary diffusion and material deformation problems as in the work of Liang and Sofronis [6].

Figure 3d shows the simulation results for the subcritical crack growth observed in the experiments of Moody *et al.* [1,2] in 207 MPa hydrogen gas. Simulations were carried out for various values of the grain boundary diffusion coefficient D_{int} for hydrogen. Whereas the assumed magnitude of the diffusion coefficient along the grain boundary affects the time at which the crack is arrested, it has no effect on the distance the crack travels. The calculated threshold stress intensity K_{th} is about $40 \text{ MPa}\sqrt{\text{m}}$; the experimentally measured value is $33.5 \text{ MPa}\sqrt{\text{m}}$ (Figure 3c).

ii) *Hydrogen-induced void coalescence and crack initiation:* We studied crack/inclusion interactions under small scale yielding conditions by considering multiple circular debonded inclusions located on the axis of symmetry ahead of a crack, as shown in Figure 4a, in the presence of hydrogen. We assumed that the inclusions are completely debonded (from the manufacturing process) and hydrogen can diffuse along the matrix/inclusion interface. In particular, we studied the cases of inclusions with volume fractions $f_0 = 0.001$, 0.0025 , and 0.00875 . We switched on hydrogen uptake through the crack faces while at the same time we began loading the domain at a constant stress intensity factor rate $K_I = 1.0 \text{ MPa}\sqrt{\text{m/s}}$.

Hydrogen induced softening was modeled as in the work of Dadfarnia *et al.* [7] in which the flow stress of the material was considered to decrease linearly with the amount of hydrogen trapped at dislocations. The numerical simulations were carried out for the C type steel whose material properties are reported in previous annual progress reports. On the crack faces a concentration $C_0 = 2.659 \times 10^{22} \text{ H atoms/m}^3$ ($= 3.142 \times 10^{-7} \text{ H atoms per solvent atom}$) in equilibrium with gas pressure of 15 MPa was prescribed.

We considered that crack initiation took place when the void nearest to the crack tip coalesced with the crack

tip. Coalescence occurs when the size of the ligament between the crack tip and the void is reduced to half its size in the undeformed state [8]. We found that hydrogen reduces the fracture toughness measured in terms of J_{IC} by about 30% at small initial void volume fraction ($f_0 = 0.001$ and 0.0025) and by 22% at $f_0 = 0.00875$. In the absence of hydrogen and at the smallest initial void volume fraction ($f_0 = 0.001$), the void closest to the crack tip experiences a significant growth in size as shown in Figure 4b while the rest of the voids do not grow significantly, a crack growth mechanism that is controlled by a single void. On the other hand, at the largest initial void volume fraction $f_0 = 0.00875$, crack growth is governed by a multiple-void growth mechanism, i.e., all three voids start growing almost simultaneously upon the application of the load at almost the same rate. In general, hydrogen increases the void growth rate irrespective of the initial void volume fraction and intensifies plastic flow localization (Figure 4c).

iii) *Transferability of fracture toughness results from laboratory specimens to the real-life pipeline:* In our previous annual progress reports, we presented the hydrogen concentration fields close to the crack tip of an axial pipeline crack. The pipeline was loaded mechanically by the hydrogen pressure exerted on the inside surface and the crack flanks while hydrogen diffused toward the outside surface. We termed the associated solution to the hydrogen transport problem

FIGURE 4. a) Model schematic used to investigate the behavior of debonded MnS inclusions in the neighborhood of a crack tip under small scale yielding conditions for a medium strength steel; b) void growth in the absence of hydrogen; c) void growth and plastic flow localization close to the crack tip in the presence of hydrogen-induced softening. In both cases (b) and (c) the remote stress intensity factor is $K_I = 89 \text{ MPa}\sqrt{\text{m}}$ and 89 s have passed from the application of the load. Hydrogen uptake was by diffusion through the crack faces.

as the full-field solution. We demonstrated that this full-field solution close to the crack tip can also be described by a modified boundary layer formulation using the T -stress the pipeline crack experiences.

Prompted by these results, we solved the initial/boundary value problem of transient hydrogen diffusion coupled with material elastoplasticity directly in a single edge notch tension specimen with a shallow crack loaded by remote tension. We chose the dimensions of the specimen and the applied tension stress such that the stress intensity factor K_I and T -stress are the same as for the axial crack in the pipeline under a given hydrogen pressure. The numerical simulations indicate that the associated stresses and deformation are almost identical. With regard to the steady-state hydrogen concentration profiles there is only a 2% difference between the full-field and the single edge notch tension specimen solutions at the location of the peak NIRS hydrogen concentration. In addition, we found that the results close to the crack tip are not affected by the remote hydrogen boundary conditions, that is, impermeable vs. an outgassing outside surface.

The simulations described in this section are essential prerequisites toward meeting all objectives of our project.

First-Principles Assessment of Hydrogen Effects on Interfacial Cohesion

Ab initio density-functional-theory calculations can reveal directly the key bonding and surface-energy effects (grain boundary, free surface, or interphase boundaries) that control interfacial cohesion in the presence of hydrogen solute atoms.

We are continuing our work to quantitatively characterize the cohesive properties of the MnS/ferrite matrix interface. The objective here is to characterize the magnitude of the component of the cohesive stress normal to the interface and whether the component tangential to the interface is negligible either due to manufacturing process effects (cooling from high temperature to ambient) or due to hydrogen accumulated at the interface.

The issue here is that in steel pipelines for the existing natural gas system sulfides and large particles provide fracture initiation sites (all project objectives).

Conclusions and Future Directions

- Hydrogen transport simulations have been carried in which material deformation is coupled to hydrogen-induced degradation in the form of grain boundary decohesion or hydrogen-accelerated void growth, respectively, for subcritical crack growth or rising load fracture toughness.

- We demonstrated that the single edge notch tension specimen can be used to experimentally measure the fracture resistance of materials as affected by hydrogen. The specimen exhibits the same constraint characteristics as cracks in real-life pipelines.
- A permeation measurement apparatus has been built and tested. Identification of the diffusion characteristics (e.g. permeability, solubility, trap strength and density) of existing and new pipeline steel microstructures is carried out with increasing membrane thickness to isolate and understand potential surface adsorption related effects.
- We completely characterized almost all materials provided by DGS Metallurgical Solutions Inc. and sample specimens taken from hydrogen pipelines operated by Air Liquide.
- We use ab initio calculation results to calibrate thermodynamic models of interfacial decohesion needed for finite element simulations of the hydrogen effect at the macroscale.
- In collaboration with Sandia National Laboratories, we carry out fracture testing along with FIB, SEM, and TEM studies to identify the failure mechanisms and associated microstructural features in the presence of hydrogen.
- Once the fracture testing results become available and the hydrogen-induced fracture mechanisms in pipeline steels are understood, we plan to integrate ab-initio calculation results through the thermodynamic theory of decohesion with finite element simulations at the continuum level in order to establish fracture criteria for pipeline safe operation.
- We continue our collaboration with the National Institute for Hydrogen Industrial Use and Storage (HYDROGENIUS) of Japan.

Special Recognitions & Awards/Patents Issued

- P. Sofronis visited Japan from June 9 to June 25, 2006 as a fellow of the Japan Society for the Promotion of Science (JSPS) to collaborate on research related to hydrogen material compatibility.
- P. Sofronis and I. Robertson were invited speakers at the *International Hydrogen Energy Development Fora* organized by HYDROGENIUS at Fukuoka, Japan on January 31 – February 1, 2007, February 4–8, 2008, February 4–6, 2009.
- P. Sofronis has been elected a fellow of the American Society of Mechanical Engineers (ASME) for his contributions to the field of hydrogen embrittlement.
- I. Robertson was an invited keynote speaker at the 7th International Conference on the Effects of Hydrogen on Materials, Grant Teton National Park, Jackson Lake Lodge, Wyoming, September 7–10, 2008.

FY 2009 Publications/Presentations

Publications

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Presentations

- Robertson, I. (2008, keynote) Revealing the Fundamental Processes Controlling Hydrogen Embrittlement,” International Symposium on the *Effects of Hydrogen on Materials*, Grant Teton National Park, Jackson Lake Lodge, Wyoming, September 7-10, 2008.
- Sofronis, P. (2008, invited) A Combined Applied Mechanics/Materials Science Approach Toward Understanding the Role of Hydrogen on Material Degradation in Low and High Strength Steels. *ExxonMobil Research and Engineering Company*, Annandale, New Jersey, April 23.
- Dadfarnia, M. Sofronis, P., Somerday, B., Biao, J., Johnson, D. (2008) Modeling Hydrogen-Induced Sustained-Load Cracking by Intergranular Failure. International Symposium on the *Effects of Hydrogen on Materials*, Grant Teton National Park, Jackson Lake Lodge, Wyoming, September 7–10.
- Sofronis, P. (2009, invited) Materials for the Hydrogen Economy: Embrittlement and Remediation. *Society of Engineering Science*, 45th Annual Technical Meeting, Urbana, Illinois, October 13–15.
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- Sofronis, P. (2009, invited) On the Design of Steel Pipelines against Hydrogen Embrittlement. *Third International Hydrogen Energy Development Forum*, Hotel Okura, Fukuoka, Japan, Feb. 4.
- Ritchie, R.O. and Sofronis, P. (2009, invited) Micro-Mechanical Modeling of Hydrogen-Induced Brittle Fracture. *Third International Hydrogen Energy Development Forum*, Hotel Okura, Fukuoka, Japan, Feb. 4.
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III.20 Hydrogen Permeability and Integrity of Steel Welds

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Project Start Date: May 1, 2004

Project End Date: September 30, 2010

Technical Targets

This project is to develop the scientific understanding, technical basis and cost-effective engineering solutions to control and mitigate hydrogen embrittlement in the steel weld region of pipelines and other high-pressure hydrogen delivery infrastructure systems. Insights gained from this project will be applied toward the hydrogen delivery infrastructure that meets the following DOE 2017 hydrogen pipeline delivery targets:

- Capital cost: \$490K/mile for transmission pipeline and \$190K/mile for distribution pipeline.
- Cost of delivery of hydrogen <\$1.00/gasoline gallon equivalent (gge).
- Reliability/Integrity: Acceptable for H₂ as a major energy carrier.

Objectives

- Quantify the effects of welding and joining on the resistance to hydrogen embrittlement (HE) of high-strength pipeline and other structural steels under high-pressure hydrogen.
- Determine the hydrogen transport behavior (absorption, diffusion, trapping, etc.) in steels.
- Develop the technical basis and guidelines to manage hydrogen, stress and microstructure in the weld region to ensure structural integrity and safety of hydrogen delivery systems.
- Develop welding/joining technology that greatly reduces the capital cost and eliminate HE concerns in constructing new pipelines and converting existing pipelines for high-pressure hydrogen delivery.
- Develop risk assessment based approach to manage the integrity and safety of hydrogen pipelines including weld joints.

Technical Barriers

This project addresses the following technical barriers from the Delivery section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (D) High Capital Cost and Hydrogen Embrittlement of Pipelines
- (F) Gaseous Hydrogen Storage and Tube Trailer Delivery Costs
- (G) Storage Tank Materials and Costs
- (K) Safety, Codes and Standards, Permitting

Accomplishments

- Baseline measurements of hydrogen permeation, diffusion and trapping in pipeline steels have been completed. Preliminary investigations on the effects of weld microstructure on the previously mentioned hydrogen transport behavior have been completed.
- Initial studies on friction stir welding of pipeline steels have completed. The results indicated considerable improvement of weld toughness and strength over the conventional arc welds.
- Completed development of a new testing method specific to quantify and rank the sensitivity of different microstructures in the weld region to hydrogen embrittlement.

Introduction

The hydrogen energy delivery infrastructure will require extensive use of steels and other cost-effective structural and functional materials under high-pressure gaseous hydrogen (H₂) exposure. For example, high pressure (up to 3,000 psi) hydrogen pipelines are presently considered to be one of the most cost-effective and energy-efficient means to transport very large amounts of hydrogen to much of the market as is done currently for natural gas [1]. Under high hydrogen pressures, there are concerns about HE of steel pipelines and its potential catastrophic consequences [2]. Concerns regarding HE are not limited to steel pipelines; according to a recent DOE Basic Energy Science Office report [3], HE needs to be addressed for a variety of

hydrogen storage and delivery system parts made of metallic materials that are exposed to hydrogen.

As in the case of natural gas and other energy carrier transmission pipelines, welding will be used to construct steel pipelines for high-pressure hydrogen delivery. Welding will be also widely used in fabrication of other system components for hydrogen production, storage, and delivery. However, welds in pipeline steels and other engineering materials are often the most susceptible regions to HE due to the formation of unfavorable microstructures and high tensile residual stresses. Indeed, recent studies [4] on pipeline steels have shown that the weld region exhibits delayed cracking (signature of HE) when exposed to high-pressure hydrogen gas. Furthermore, the weld region typically has substantially lower resistance to hydrogen crack initiation and higher crack growth rates, when compared to the baseline pipeline steel (base metal). *In this regard, the weld region can be the weakest link for the structural integrity and safety of hydrogen pipelines and hydrogen delivery infrastructure.* A systematic approach to deal with weld property degradation under high-pressure hydrogen gas is critical to ensure the safe, cost-effective operation and long-term reliability of the hydrogen delivery infrastructure.

Approach

While there have been extensive studies in the past on HE and hydrogen-induced material property degradation of pipeline steels, the high-pressure hydrogen delivery pipeline presents some unique issues that are seldom addressed in the past. At the center of these issues is the hydrogen transport behavior in metal – the absorption, diffusion, and trapping of hydrogen in metal. At the present time, very limited knowledge is available about the rate of diffusion and amount of hydrogen in steel under high-pressure gaseous environment relevant to the hydrogen delivery infrastructure. Therefore, the first major effort in this project is directed toward high-pressure hydrogen permeation and mechanical performance tests to systematically study the hydrogen permeation behavior and to evaluate the tolerance level to hydrogen of different steels before considerable mechanical property degradation would occur.

The weld joint in steel pipeline is expected to be a critical region mostly susceptible to hydrogen embrittlement due to the formation of unfavorable microstructure and the high residual stresses. The second major activity of this project focuses on developing new welding technology and/or improve existing welding technology to optimize weld microstructure and proactively control the weld residual stress for hydrogen pipeline construction and repair. In addition, special testing methods need to be developed to quantify the degradation of

mechanical properties in the weld region with complex microstructure and HE resistance gradients. Finally, risk assessment based approach will be developed to manage the integrity and safety of hydrogen pipelines including the weld joints.

Results

The Fiscal Year 2009 activities focused on the development of testing methods and system for quantifying the degree of weld property degradation under high-pressure hydrogen pressure.

Current standard methods for testing hydrogen-induced mechanical property degradation of base metal have shown to be inadequate for the weld metal region due to the highly inhomogeneous microstructure and property gradients of the weld region [4]. In this project, we designed and fabricated miniaturized and self-loading testing devices for in situ measurement of mechanical property degradation of weld metal in high-pressure gaseous hydrogen environments. Two types of the mechanical testing devices were devised. The first one was a special multiple-notched tensile test where the notch is precisely located in different regions of weld. This test is intended as a quick yet quantitative screening test of weld property changes under high-pressure hydrogen. The second type test was a novel fracture toughness test based on the spiral notch torsion test (SNTT) method. The compact size and self-loading mechanisms employed in both testing devices make it possible that the entire loading assembly and the test specimen be placed inside a relatively small high-pressure chamber. This minimizes the capital cost of the testing system and allows for multiple testing devices to be operated in a single high-pressure vessel to cost-effectively study and quantify the effects of the weld microstructure on HE resistance of different steels. The effects of high-pressure hydrogen on the stability of load sensors immersed in hydrogen have been solved with a novel sensor design.

In FY 2009, we focused on the development of the in situ SNTT method under high-pressure hydrogen. A unique miniature self-loading device was successfully developed that can be placed inside the autoclave. The long-term stability of the load-monitoring system with temperature and pressure self-compensation capability and resistance to hydrogen permeation was successfully evaluated under high-pressure hydrogen. Figure 1 shows the design of the spiral notch specimen

FIGURE 1. SNTT specimen for K_{th} Measurement under High-Pressure Hydrogen

used in this project for fracture toughness threshold (K_{th}) measurement under high-pressure hydrogen environment. A U.S. patent application has been submitted for the in situ SNTT method under high-pressure hydrogen developed in this project.

In addition, a 3-dimensional finite element model has been developed to determine the stress intensity factor for the specific SNTT configuration used in this work. Figure 2 shows the circumferential stress (Mode I stress) distribution in the specimen, from which the stress intensity can be calculated. This model will be used to calculate K_{th} for high-pressure hydrogen embrittlement test planned in next quarter.

The validity of the SNTT method was first confirmed by testing American Iron & Steel Institute (AISI) 4340 steel in air, by comparing with the fracture toughness (K_{IC}) results of Bandyopadhyay et al. [5] on the same steel obtained using the standard compact tension (CT) specimen. It is important to note that, in order to compare with the CT testing results, the entire SNTT specimen was heat-treated to a uniform microstructure by furnace heating and oil quenching. The AISI 4340 steel was heat treated to fully hardened microstructure with hardness of 50-53 Rockwell Scale C, following the heat treatment procedure by Bandyopadhyay. The K_{IC} value from the SNTT was averaged at 67.5 ksi-in^{1/2}, which is consistent with reported 65-75 ksi-in^{1/2} by standard CT specimen.

Under 2,000 psi high-pressure hydrogen, the threshold fracture toughness for crack initiation (K_{th}) reduced to 36–39 ksi-in^{1/2} (obtained from multiple samples). The reduction is about 55% of K_{IC} values in air. The broken sample shown in Figure 3 confirmed that the Mode I fracture is achieved in the SNTT test under high-pressure hydrogen.

FIGURE 2. Circumferential Stress Distribution in SNTT Specimen

FIGURE 3. Broken SNTT Specimen Tested in High-Pressure Hydrogen for K_{th} Measurement

In addition, SNTT steel specimens with non-uniform microstructure distributions were produced with the Gleeble thermophysical simulator. These specimens will be tested in air and in high-pressure hydrogen to study the effect of inhomogeneity of microstructure/property on fracture toughness of steels. SNTT specimens made from actual welded pipelines will be then tested to determine the degree of property degradation of pipeline steel welds under high-pressure hydrogen.

In summary, we have successfully demonstrated the SNTT method for K_{th} testing under high-pressure hydrogen. The SNTT test has been performed using uniform microstructure specimen. We will continue to develop the SNTT method to test non-uniform microstructures in the heat-affected zone and weld region in the remaining of the project. The research on weld property testing under high-pressure hydrogen environment in this project has resulted in three U.S. patent applications in FY 2009.

Conclusions and Future Directions

This project focuses on the resistance of HE in the weld region of steels, the region regarded as the weakest link for the structural integrity and safety of hydrogen pipeline and hydrogen delivery infrastructure. We have accomplished the followings milestones in FY 2009:

- Baseline measurements of hydrogen permeation, diffusion and trapping in pipeline steels and preliminary investigations on the effects of weld microstructure on hydrogen transport.
- Initial work on friction stir welding on pipeline steels which showed considerable improvement of weld toughness and strength over the conventional arc welds.
- Development of a new testing method specific to quantify and rank the sensitivity of different microstructures in the weld region to hydrogen embrittlement.

The project plan for FY 2010 includes (1) develop the understanding and the relationship between hydrogen permeation and diffusion and various microstructures in pipeline steels, (2) continue on welding technology development to reduce the weld residual stress and manage the weld microstructure to improve the resistance to HE, and (3) complete the

development of testing methods to quantify the HE resistance in the weld region under both static and cyclic loading conditions.

Special Recognitions & Awards/Patents Issued

Three U.S. patent applications have been filed in FY 2009 in this project on the subject of weld mechanical property testing under high-pressure hydrogen subjecting to static and low-cycle cyclic loading conditions.

FY 2009 Publications/Presentations

1. Feng, Z. Steel, R. Packer, S. and David, S.A. 2009. "Friction Stir Welding of API Grade 65 Steel Pipes." – ASME PVP Conference, Prague, Czech Republic.
2. Feng, Z. Anovitz, L.M., Armstrong, T.A. 2009. "hydrogen permeation and diffusion in steels under high pressure hydrogen (Invited)." – TMS Annual Meeting, San Francisco, CA.
3. 2009 DOE Hydrogen Program Review – Washington, DC, May 2009. PDP 43.

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3. U.S. Department of Energy, "Basic Research Needs for the Hydrogen Economy," *Basic Energy Sciences Workshop on Hydrogen Production, Storage, and Use*, Second Print, February, 2004.
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III.21 Hydrogen Embrittlement of Structural Steels

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Project Start Date: January 2007
Project End Date: Project continuation and
direction determined annually by DOE

The salient reliability/integrity issue for steel hydrogen pipelines is hydrogen embrittlement. One particular unresolved issue is the performance of steel hydrogen pipelines that are subjected to extensive pressure cycling. One of the objectives of this project is to enable safety assessments of steel hydrogen pipelines subjected to pressure cycling through the use of structural integrity models.

Accomplishments

- Measured tensile properties of X52 and X100 pipeline steels in hydrogen gas as part of the DOE Pipeline Working Group materials-testing round robin.
- Demonstrated ability to measure fatigue crack growth rates of pipeline steels in high-pressure hydrogen gas using new laboratory capability.

Objectives

1. Enable application of structural integrity models to steel hydrogen pipelines:
 - Measure fatigue crack growth rates and rapid-cracking thresholds of line pipe steels in high-pressure hydrogen gas.
 - Apply structural integrity model coupled with steel properties measured in hydrogen gas to assess performance of steel pipeline.
2. Enable development of micromechanics models of hydrogen embrittlement in pipeline steels:
 - Establish physical models of hydrogen embrittlement in line pipe steels using evidence from analytical techniques such as electron microscopy.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Delivery section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (D) High Capital Cost and Hydrogen Embrittlement of Pipelines
- (G) Storage Tank Materials and Costs

Technical Targets

The principal target addressed by this project is the following (from Table 3.2.2):

- Reliability/Integrity

Introduction

Carbon-manganese steels are candidates for the structural materials in hydrogen gas pipelines, however it is well known that these steels are susceptible to hydrogen embrittlement. Decades of research and industrial experience have established that hydrogen embrittlement compromises the structural integrity of steel components. This experience has also helped identify the failure modes that can operate in hydrogen containment structures. As a result, there are tangible ideas for managing hydrogen embrittlement in steels and quantifying safety margins for steel hydrogen containment structures. For example, fatigue crack growth aided by hydrogen embrittlement is a key failure mode for steel hydrogen containment structures subjected to pressure cycling. Applying appropriate structural integrity models coupled with measurement of relevant material properties allows quantification of safety margins against fatigue crack growth in hydrogen containment structures. Furthermore, application of these structural integrity models is aided by the development of micromechanics models, which provide important insights such as the hydrogen distribution near defects in steel structures.

Approach

The principal objective of this project is to enable application of structural integrity models to steel hydrogen pipelines. The new American Society of Mechanical Engineers (ASME) B31.12 design code for hydrogen pipelines includes a fracture mechanics-

based design option, which requires material property inputs such as the threshold for rapid cracking and fatigue crack growth rate under cyclic loading. Thus, one focus of this project is to measure the rapid-cracking thresholds and fatigue crack growth rates of line pipe steels in high-pressure hydrogen gas. These properties must be measured for the base materials but more importantly for the welds, which are likely to be most vulnerable to hydrogen embrittlement. The measured properties can be evaluated by predicting the performance of the pipeline using a relevant structural integrity model, such as that in ASME B31.12.

A second objective of this project is to enable development of micromechanics models of hydrogen embrittlement in pipeline steels. The focus of this effort is to establish physical models of hydrogen embrittlement in line pipe steels using evidence from analytical techniques such as electron microscopy. These physical models then serve as the framework for developing sophisticated finite-element models, which can provide quantitative insight into the micromechanical state near defects. Understanding the micromechanics of defects can ensure that structural integrity models are applied accurately and conservatively.

Results

A materials-testing round robin was coordinated by the DOE Pipeline Working Group with the objective of demonstrating that three participants (Sandia National Laboratories/California, Oak Ridge National Laboratory, and the National Institute of Standards and Technology) can provide reliable data on the mechanical properties of ferritic steels measured in high-pressure hydrogen gas. The emphasis for this round robin was measurement of tensile properties for two line pipe steels.

The tensile test matrix consisted of two steels (X52 and X100) and three environmental conditions (hydrogen gas, helium gas, and air). The steel products and tensile specimens were procured by Concurrent Technologies Corporation (a participant in the Pipeline Working Group) and supplied to the three laboratories. The intent of the test matrix was to produce triplicate results for each combination of steel and test environment. Sandia modified the test matrix to produce an initial set of duplicate results for each combination of steel and test environment. The reason for the modification was due to sub-optimal performance of the load cell located internal to the pressure vessel. It was decided to execute only part of the test matrix with this load cell, and the balance of the test matrix would be completed once the load cell performance was improved.

The modified test matrix was executed following procedures developed by participants in the round

robin. Test procedures that were defined included the hydrogen and helium gas test pressures (14 MPa), the tensile strain rate (10^{-4}), and the test temperature (room temperature). Sandia successfully conducted the testing following the specified procedures, although two aberrations were noted. First, the gas pressure during testing in hydrogen and helium was not constant, but varied over about 1 MPa from the nominal pressure of 14 MPa. This pressure variation was due to gas leaks at the sliding seals in the pressure vessel. The second issue was apparent inaccurate labeling of some tensile test specimens. Specifically, two specimens labeled as X52 were evidently the other steel, X100. These aberrations did not affect the quality or reliability of the results.

Four properties were measured from the tensile tests, as summarized in Table 1: yield strength (S_y), ultimate tensile strength (S_u), elongation to fracture (EI), and reduction of area at fracture (RA). These tensile properties were defined and measured following procedures outlined in ASTM International standards. The elongation to fracture was based on measurements of the original and final overall lengths of the tensile specimens. The gauge length for these measurements was approximately the gauge section of the tensile specimen (19 mm).

TABLE 1. Tensile properties of X52 and X100 line pipe steels measured in air, helium, and hydrogen.

Steel	Environment	S_y (MPa)	S_u (MPa)	EI (%)	RA (%)
X52	air	429	481	31	79
X52	air	431	488	29	80
X52	helium	417	486	31	75
X52	helium	423	481	30	76
X52	hydrogen	430	495	24	49
X52	hydrogen	423	486	24	60
X100	air	769	919	20	74
X100	air	725	856	21	78
X100	helium	719	878	20	79
X100	helium	787	882	21	77
X100	hydrogen	755	914	13	38
X100	hydrogen	791	897	13	38

The data in Table 1 demonstrate some expected trends. The yield and tensile strengths of the X100 steel are significantly greater than strengths for the X52 steel. In addition, hydrogen degrades the ductility (elongation or RA) of both steels. The effect of hydrogen on ductility is more pronounced for the high-strength X100 steel. Other notable trends are that data for tests conducted in air and helium are similar and data are consistent within each set of duplicate tests.

The laboratory capability for measuring fatigue crack growth rates of structural metals in high-pressure hydrogen gas was completed and initial testing was successfully demonstrated. The initial fatigue crack growth testing focused on the X100 steel from the round robin. A compact tension specimen fabricated from X100 was tested in 21 MPa hydrogen gas at a load cycle frequency of 1 Hz and a load ratio ($R = \text{minimum load}/\text{maximum load}$) equal to 0.5. The test was executed by imposing a sinusoidal loading wave form on the test specimen at fixed values of maximum load and minimum load, which resulted in an increasing stress-intensity factor range (ΔK) as the crack extended. The crack growth rate per load cycle (da/dN) measured as a function of applied ΔK is plotted in Figure 1. In this figure, the data measured in hydrogen gas are compared to another set of data measured in air. The data clearly demonstrate the effect of hydrogen on accelerating fatigue crack growth rates of steels. Although hydrogen has such a pronounced effect on fatigue crack growth rates, measurements such as those in Figure 1 enable the implementation of structural integrity models (e.g., Option B in ASME B31.12) that accommodate manifestations of hydrogen embrittlement.

FIGURE 1. Fatigue crack growth rate per load cycle (da/dN) vs stress-intensity factor range (ΔK) data for X100 steel in hydrogen gas and air.

Conclusions and Future Directions

- Measurements of tensile properties for the materials-testing round robin and fatigue crack growth rates represent progress toward assuring reliability/integrity of steel pipelines for hydrogen gas service.
- (future) Measure the fatigue crack growth rates of technologically important pipeline steels such as X42 and X52 in high-pressure hydrogen gas. These measurements must be conducted on the base metal as well as welds.

FY 2009 Publications/Presentations

1. (invited presentation) "Fracture Control of Hydrogen Containment Components", B. Somerday, *International Hydrogen Energy Development Forum 2009*, Fukuoka, Japan, Feb. 2009.
2. "On the Small Scale Character of the Stress and Hydrogen Concentration Fields at the Tip of an Axial Crack in Steel Pipeline: Effect of Hydrogen-Induced Softening on Void Growth", M. Dadfarnia, P. Sofronis, B. Somerday, I. Robertson, *International Journal of Materials Research*, vol. 99, 2008, pp. 557-570.
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III.22 Geologic Storage of Hydrogen

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Project Start Date: May 1, 2007
Project End Date: September 30, 2009

Objectives

To determine the suitability and availability of underground geologic storage for hydrogen by 1) developing a white paper that will present an understanding of geologic storage types and by 2) analyzing the costs to develop and operate these various storage sites. The paper will describe:

- Different storage types
- Advantages and disadvantages of the different storage types
- Maps of locations where storage is available
- Operational issues specific to hydrogen

The economic analyses will address:

- Development costs
- Plant costs
- Operational costs

Technical Barriers

This project addresses the following technical barrier from the Hydrogen Delivery section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

(H) Geologic Storage

Technical Targets

This project will present an understanding of the various types of underground geologic storage available and their suitability for the storage of hydrogen. An economic analysis will portray the potential costs

entailed in developing and operating the most viable candidates for the underground storage of hydrogen. This information and analyses will help DOE achieve its technical target for Geologic Storage as presented in Table 1.

TABLE 1. DOE Technical Target for Geologic Caverns

Category	Current Status	2017 Target
Installed Capital Cost	Assumed equal to natural gas	Equal to natural gas caverns

Accomplishments

Fiscal Year 2008

- Wrote a white paper describing the various types of underground geologic storage options available for the storage of natural gas.
- Produced four location maps showing the available underground storage sites in the United States (U.S.).
- Identified the three most likely geologic candidates for the underground storage of hydrogen, these being, 1) salt caverns, 2) depleted gas reservoirs, and 3) aquifers.
- Identified possible issues with storing hydrogen in geologic formations that may need to be addressed:
 - Hydrogen embrittlement
 - Hydrogen mobility
 - Gas mixing
 - Chemical reactions
 - Effect on rock properties

Fiscal Year 2009

- Performed an economic analysis on salt caverns, which are one of three geologic underground sites being considered for the storage of hydrogen. An in depth analysis included:
 - Site development costs
 - Plant costs
 - Operational costs
- Currently developing an economic analysis for both 1) depleted oil/gas reservoirs, and 2) aquifers, which, are the two additional types of storage sites being considered for the underground storage of hydrogen. Analyses will be complete by September 2009.

Introduction

The concept of storing natural gas underground in geologic formations arose from the need to supply gas to consumers during periods of high seasonal demand. The storage of natural gas is also an insurance policy against accidents and natural disasters. There are currently several types of underground storage used for natural gas with the three prominent types being depleted gas reservoirs, aquifers, and mined salt caverns. Understanding these various geologic storage types will help identify what geologic option would be best suited for the storage of hydrogen. Currently there are only three locations worldwide, two of which are in the United States, which store hydrogen. All three sites store hydrogen within salt caverns.

The project has an interest in understanding these types of underground storage options in the hopes of developing an underground facility for the storage of hydrogen, as a low-cost storage option, as part of the hydrogen delivery infrastructure. To date a white paper has been written that gives an overview of the various types of geologic storage currently in use for the storage of natural gas. The intent is to give an understanding of geologic storage, to describe the different storage types, and to state the advantages and disadvantages of the underground facilities as they relate to natural gas and subsequently hydrogen gas. To achieve the project's geologic cavern technical objective an economic analysis tool is currently being developed for three underground storage options that will help ensure capital costs will be similar to those of natural gas storage.

Approach

To achieve the first project objective, which entailed writing a paper describing underground geologic storage, an extensive literature search was conducted. The goal of the literature search was to collect information pertaining to 1) the underground geologic storage options currently in use for natural gas, 2) possible alternative storage options currently being tested, 3) the advantages and disadvantages of each option, 4) the location of these storage types, 5) the possible problems that may arise with the storage of hydrogen versus natural gas, and 6) current examples of underground facilities storing hydrogen gas.

The second objective – analyzing the costs to develop and operate various storage sites – will be achieved by creating an analysis based on a user-friendly computer model built in Powersim Studio®. The tool is used in scenario mapping of development costs, plant costs, and operational costs of underground hydrogen storage for salt caverns. Cost analyses for both depleted gas/oil reservoirs and aquifers will be complete by the end of FY 2009.

Results

White Paper

The outcome of the literature search and resulting paper provides an understanding of the underground storage options available for hydrogen. In many regions across the nation geologic formations are currently being used to store natural gas underground. Natural gas is stored to meet seasonal demands and to protect against accidents and natural disasters that could cause a disruption in supply. Storage of natural gas is used to meet both base load and peak load requirements. Storage options are dictated by the regional geology and the operational need.

Currently, depleted gas/oil reservoirs, aquifers, and salt caverns are the three main types of underground natural gas storage in use today. The other storage options available currently and in the near future, such as abandoned coal mines, lined hard rock caverns, and refrigerated mined caverns, will become more popular as the demand for natural gas storage grows, especially in regions where depleted reservoirs, aquifers, and salt deposits are not available.

Underground storage must have adequate capacity and containment of gas. The storage formation must have high permeability in order for gas to be injected and extracted at adequate rates. Porous reservoirs such as depleted gas reservoirs and aquifers must possess an impermeable caprock along with a geologic structure to contain and trap gas. Mined caverns such as salt caverns contain gas by the impermeability of the surrounding host rock.

Aquifers and depleted reservoirs possess the largest capacity and require the greatest volume of cushion gas. The reservoirs are typically cycled once annually and are used to meet base load demand. Unlike depleted reservoirs aquifers must be proven to trap and contain gas.

Salt caverns are solution mined and hold a fraction of the gas volume than that of depleted reservoirs and aquifers. Salt caverns are typically used to meet peak load demands by possessing multi-cycle capabilities and providing high delivery rates.

Excavated caverns within rocks such as coal and granite contain volumes less than aquifers and depleted reservoirs and are generally developed in regions where reservoirs are not available. Excavated caverns by nature are not completely impervious to gas loss. Several techniques have been developed to insure gas containment, such as lining caverns with steel and increasing the hydraulic pressure surrounding the caverns.

The storage of hydrogen within the same type of facilities, currently used for natural gas, may add new operational challenges to the existing cavern storage

industry, such as the loss of hydrogen through chemical reactions and the occurrence of hydrogen embrittlement. However, it has been shown that if the underground storage of hydrogen is operated at pressures below 1,200 psi and at temperatures below 500°F there may be little need for concern. It is encouraged that all steel used in the storage and operation of a site be free of defects and possess low-yield strength.

In the U.S. two companies, ConocoPhillips and Praxair, currently store hydrogen underground. The hydrogen is stored in salt caverns, both which are located within the Clemens salt dome in Texas.

Economic Analysis

As a generalization, aquifers cost the most to develop and operate. The major costs contributing are the large cushion gas requirements and the need to verify the reservoir's capability to contain gas. Depleted gas/oil reservoirs may be more economical to develop because the sites contain existing infrastructure and gas containment is proven. Salt caverns are likely the most economical, due to their multi-cycle capabilities and high annual throughput of gas. Salt caverns are typically used to meet peak load demands. However, in

order for DOE to achieve its technical target for geologic storage a cost model is currently being developed to analyze in greater detail the potential costs entailed in developing and operating the most viable candidates for the underground storage of hydrogen.

The economic model, created using Powersim Studio®, will be used to perform economic analyses on the three types of storage sites being considered for hydrogen, salt caverns, depleted reservoirs, and aquifers. Currently, the model framework is complete for analyzing costs, both capital and operational, associated with developing and operating underground salt caverns. The model interface allows the user to adjust parameters to fit their storage needs, such as 1) cavern/reservoir size, 2) compressor size, and 3) cushion gas requirements. Figure 1 displays an example of the model interface for the salt cavern model. Figure 2 is the user interface for compressor costs, whereas Figure 3 is the interface displaying inventory results. The framework and subsequent model's development will be modular by design, allowing it to be used in other larger hydrogen infrastructure assessment models.

Cost analyses for both depleted gas/oil reservoirs and aquifers will be complete by the end of FY 2009.

FIGURE 1. Salt Cavern Model Cost and Volume Model Interface (as of June 2009)

FIGURE 2. Salt Cavern Compressor Cost Module (as of June 2009)

FIGURE 3. Salt Cavern Inventory Model (as of June 2009)

Conclusions and Future Directions

After reviewing the storage options that are currently available for hydrogen the following conclusions have been made.

- There are three probable candidates for the underground storage of hydrogen:
 - Salt caverns
 - Depleted gas reservoirs
 - Aquifers
- Salt caverns are currently the only underground facility used to store hydrogen.
- When constructing a site, materials must be used, such as low-yield-strength steel to prevent hydrogen embrittlement and gas leaks.
- Additional research may need to be conducted in the following areas to ensure hydrogen containment and purity:
 - Hydrogen mobility
 - Hydrogen embrittlement
 - Gas mixing
 - Effect of hydrogen on rock properties

In working towards the DOE's technical target of maintaining capital costs similar to natural gas storage a cost model is currently being developed, which will enable the user to evaluate the costs entailed in

developing and operating the following underground storage facilities:

- Salt caverns (complete)
- Depleted gas reservoirs (in progress)
- Aquifers (in progress)

An in depth analysis will include:

- Site development costs
- Plant costs
- Operational costs

Future tasks will expand on the work already completed by focusing on specific alternative storage options such as lined hard rock caverns, specifically,

- Lava tubes

FY 2009 Publications/Presentations

1. Lord, A.S., P.H. Kobos, D.J. Borns, "Underground Storage of Hydrogen: Assessing Geostorage Options with a Life Cycle Based Systems Approach" presented at the 28th annual IAEE/USAE conference in New Orleans, LA, December 3–5, 2008.

2. Lord, A.S., P.H. Kobos, D.J. Borns, "Geologic Storage of Hydrogen" presented at the 2009 DOE Annual Merit Review in Crystal City, VA, May 21, 2009.

IV. HYDROGEN STORAGE

IV.0 Hydrogen Storage Sub-Program Overview

Introduction

Hydrogen Storage activities in Fiscal Year 2009 continue to focus on research and development (R&D) of low-pressure, materials-based technologies suitable to both stationary and transportation applications to allow for a driving range of more than 300 miles (500 km) while meeting packaging, cost, safety, and performance requirements to be competitive with current vehicles. Figure 1 shows the framework for DOE's National Hydrogen Storage Project. It includes independent projects and Centers of Excellence (CoEs) in applied hydrogen storage R&D as well as DOE Office of Science basic research in hydrogen storage. Materials projects are focused in three main areas: metal hydrides, chemical hydrogen storage materials, and hydrogen sorbents. The Hydrogen Storage Engineering CoE was initiated in FY 2009 to provide a coordinated approach to the engineering R&D of on-board storage and refueling systems; and marked an enhanced programmatic emphasis on systems integration, design, and prototype development. Accelerated and strengthened system analysis efforts in 2009, as well as the continuing activities in material chemical and environmental reactivity, are contributing to this programmatic emphasis.

DOE is continuing close coordination with other national and international efforts to leverage technical talent worldwide, to avoid duplication and to help accelerate progress in hydrogen storage R&D. Figure 2 shows the progress in collaborative activities and how DOE's applied R&D program (Office of Energy Efficiency and Renewable Energy, EERE) interfaces with key partners to enable the ultimate development of commercially viable hydrogen storage technologies.

FY 2009 also saw a continued close coordination with the DOE Office of Science basic research activity as well as growth in the applied R&D portfolio. Twenty nine fundamental studies on hydrogen

¹ Coordinated by DOE Energy Efficiency and Renewable Energy, Office of Hydrogen, Fuel Cells and Infrastructure Technologies

² Basic science for hydrogen storage conducted through DOE Office of Science, Basic Energy Sciences

³ Coordinated with Delivery Program element

FIGURE 1. Framework for the U.S. National Hydrogen Storage Project

FIGURE 2. Hydrogen Storage Collaborations

storage materials are being supported by the Office of Science. Within EERE, 10 new projects competitively selected in FY 2008 that focus on both new materials and new concepts were initiated this year. The organizations (and R&D topics) were: Northwestern University (multicomponent hydride mixtures), Northwestern University (porous carbons with higher hydrogen binding energy), Ohio State University (aluminoboranes), Pennsylvania State University (hydrogen spillover materials), U.S. Borax (amine borane regeneration), University of Missouri (nanoporous monolithic carbons), University of Oregon (carbon-boron-nitrogen heterocycle materials), University of California, Los Angeles (covalent organic framework and zeolite imadazolate framework nanostructured materials), Los Alamos National Laboratory (capacitive H₂ storage with dielectrics), and Sandia National Laboratories (nanoparticle synthesis via ordered polymer templates). In summary, the storage portfolio is currently comprised of 41 universities, 15 companies and 14 federal laboratories.

Goals

The sub-program's primary objective in 2009 is to develop and demonstrate viable hydrogen storage technologies for transportation and stationary fuel cell applications. There are many requirements to achieve technical success: volume, weight, cost, durability, cycle life, and transient performance as examples. Several of the original performance targets for light-duty vehicles were revised in 2009 as scheduled based on real-world experience with hydrogen fuel cell vehicles. The original 2010 and 2015 targets are compared to the new 2010, 2015, and "Ultimate" targets in Table 1. The ultimate targets are intended to facilitate the introduction of hydrogen-fueled propulsion systems across the majority of vehicle classes and models. While these targets continue to be based upon application requirements and not current storage technology capabilities, they have been updated to account for differences in vehicle architecture between gasoline internal combustion engines and fuel cell vehicles. The revised targets are based upon the packaging, design, and fuel economy of current fuel cell vehicles. These revised targets can be found at: http://www1.eere.energy.gov/hydrogenandfuelcells/storage/pdfs/targets_onboard_hydro_storage.pdf

Although automakers have recently demonstrated progress with some vehicles that can travel more than 300 miles on a single fill, this driving range must be achievable across different vehicle models and without compromising space, performance or cost. Storage materials and concepts are needed to meet

TABLE 1. Performance Targets as Revised in 2009

Target	2010	2010	2015	2015	Ultimate
	old	new	old	new	new
System Gravimetric Density [% wt.] (kWh/kg)	6 (2.0)	4.5 (1.5)	9 (3.0)	5.5 (1.8)	7.5 (2.5)
System Volumetric Density [g/L] (kWhr/L)	45 (1.5)	28 (0.9)	81 (2.7)	40 (1.3)	70 (2.3)
System fill time for 5-kg fill [min] (kg H ₂ /min)	3 (1.67)	4.2 (1.2)	2.5 (2.0)	3.3 (1.5)	2.5 (2.0)
System cost (\$/kg H ₂) (\$/kWhr _{net})	133 (4)	133* (4)*	67 (2)	67* (2)*	tbd

*Cost targets are still being considered as other H₂-fuel cell vehicle targets are assessed.

the 2015 and ultimate targets to enable market penetration of hydrogen-fueled vehicles that can achieve greater than a 300-mile driving range without compromising packaging, cost, safety, and performance.

In 2009 DOE will also address storage options to facilitate EERE objectives for deployment and market growth of fuel cell power packs for early market applications with stationary, portable, and back-up power systems. Efforts will be initiated to identify key challenges, priorities and needs for these applications.

FY 2009 Technology Status

Hydrogen storage for on-board transportation applications remains one of the most technically challenging barriers to the widespread commercialization of hydrogen vehicles. On-board hydrogen storage approaches under investigation include high capacity metal hydrides, high surface area sorbents, chemical hydrogen storage carriers, low-cost and conformable tanks, compressed/cryogenic hydrogen tanks, and new materials or processes, such as conducting polymers, spillover materials, metal organic frameworks (MOFs), and other nanostructured materials. There are two principal classes of on-board storage systems. “On-board reversible” systems can be refueled on-board the vehicle from a hydrogen supply at the fueling station. These include physical storage systems, such as compressed/cryogenic tanks, as well as on-board reversible material systems such as metal hydrides and high surface area sorbents. “Regenerable off-board” systems involve materials that are not easily and quickly “refilled” or regenerated with hydrogen while on-board the vehicle. These include chemical hydrogen storage materials and certain metal hydrides where the temperature, pressure, kinetics, and/or energy requirements are such that the processes must be conducted off-board the vehicle.

The current storage *system* status values are shown relative to the revised 2015 and ultimate targets in Figure 3. The points and ranges shown are estimates provided by developers and by the R&D community and continue to be updated as new data become available. Because a very limited number of publicly available complete full-scale systems have been fabricated, most of the data shown are projections based on system design analysis or on laboratory sub-scale prototypes. Key exceptions to this are the ranges for 350 and 700 bar compressed hydrogen tanks, which show actual system data from the DOE Learning Demonstration Project, part of the Technology Validation sub-program involving 140 hydrogen fuel cell vehicles. The majority of these vehicles used 5,000 psi (350 bar) hydrogen tanks (system gravimetric and volumetric capacities of 2.8-3.8 wt% and 17-18 g/L, respectively). Over 30 demonstrations used 10,000 psi (700 bar) where the storage system capacities ranged from 2.5-4.4 wt% and 18-25 g/L. The driving range for many second generation demonstration vehicles, based on Environmental Protection Agency driving cycle data, was 196 to 254 miles. Although cryogenic systems (e.g. cryo-compressed and liquid H₂) are approaching or meeting the revised 2010 targets, it is clear that none of the current systems actually meet the combined gravimetric and volumetric system targets for 2015. It should also be reiterated that there are several other requirements such as cost, hydrogen charging and discharging rates, durability, etc., that are not illustrated in Figure 3 and that must be met simultaneously with the capacity targets.

FIGURE 3. 2009 Status of Hydrogen Storage Systems versus Revised 2015 Targets

FY 2009 Accomplishments

During FY 2009, a number of new materials were developed and the performances of earlier materials improved through the materials CoE and independent projects. Down-select decisions were made and materials eliminated based on performance criteria so that work could be focused on more promising directions. At the end of FY 2007 approximately 55 materials were considered within the Metal Hydride CoE (MHCoE) and work on about 60% of those was discontinued based on criteria developed by the MHCoE that included material reversible capacity, sorption thermodynamics and kinetics.¹ During the past year, the down selection process was continued by the MHCoE as more materials were prepared and characterized. Examples of the criteria for discontinuing evaluation of several of these materials include: unacceptably high desorption temperature ($\text{Ca}(\text{BH}_4)_2$); irreversibility ($\text{Na}_2\text{Zr}(\text{BH}_4)_6$, $\text{LiMn}(\text{BH}_4)_6$, $\text{Li}_2\text{Zr}(\text{BH}_4)_6$, $\text{NaMn}(\text{BH}_4)_6$, $\text{LiSc}(\text{BH}_4)_4$); and excessive ammonia release ($\text{LiCa}(\text{BH}_4)_3\cdot\text{NH}_3$). The remaining hydride materials systems still under investigation by the MHCoE include: $\text{LiBH}_4/\text{MgH}_2$ in aerogels, LiMgN , $\text{Mg}(\text{BH}_4)_2$, $\text{Mg}(\text{BH}_4)_2\cdot(\text{NH}_3)_2$, $\text{MgH}_2\text{-Ti}$, AlH_3 , LiAlH_4 , $\text{LiBH}_4/\text{Mg}_2\text{NiH}_4$, and other new systems involving combinations of NH_2 , BH_4 , AlH_4 , and NH_3 species.

The Chemical Hydrogen Storage CoE (CHSCoE) completed an initial down-select process during FY 2008 in which more than 60 materials were evaluated and about 50% of these materials were discontinued.² This process has continued through FY 2009 with a total of about 120 material/combinations examined and approximately 85% discontinued. Investigations of these materials or release concepts have been discontinued for reasons of low capacity, poor release kinetics, high release temperatures, or inefficient spent fuel regeneration. The remaining materials still under investigation include many derivatives of ammonia borane (AB) or mixtures of AB with additives. During FY 2009, CHSCoE research efforts have focused on improving the kinetics and capacities for hydrogen release

¹ L. Klebanoff, Materials Go/No-Go Decisions Made Within the Department of Energy Metal Hydride Center of Excellence (MHCoE) In fulfillment of the end of Fiscal Year 2007 Project Milestone on Materials Down-selection, September/October 2007, published on DOE HFCIT Website, http://www1.eere.energy.gov/hydrogenandfuelcells/pdfs/mhcoe_materials_downselect_report_fy07.pdf

² "Down Select Report of Chemical Hydrogen Storage Materials, Catalysts, and Spent Fuel Regeneration Processes," May 2008, published on DOE HFCIT Website, http://www1.eere.energy.gov/hydrogenandfuelcells/pdfs/chs_coe_down_select.pdf

through the use of catalysts and other additives for both solid and liquid phases in various AB systems. In addition, considerable effort was focused in 2009 on the continued improvement towards an energy efficient and cost-effective AB regeneration scheme. To identify areas for improvement, a major effort was made to estimate the costs for regeneration of AB from spent fuel at large-scale using the thiol process. The cost study identified the equipment and energy required for the multiple separation steps to be the dominant cost factor. Subsequently, mechanisms of various reactions of the AB regeneration process were studied and some promising alternative routes (e.g., using hydrazine during the reduction process) with the potential to reduce the number of necessary separations to improve efficiency and lower costs were identified.

A down-select process was completed by the Hydrogen Sorption CoE (HSCoE) during FY 2009 on approximately 60 materials with about 40 being discontinued. A report on these results is now in preparation. In depth modeling studies were performed within the HSCoE to better characterize the hydrogen spillover process and understand the mechanisms in order to facilitate the diffusion and transfer processes between the metal catalysts and substrates. Improved capacities and kinetics were obtained in some systems although reproducibility remains a challenge that is being addressed. The maximum room temperature capacity reproduced to date for spillover on activated carbon is 1.2 wt%. New carbon materials with narrow pore size distributions (i.e., pores in range of 0.5 - 1.0 nm) and larger binding energies were prepared and evaluated.

Significant R&D is needed to modify or “tune” the properties of high hydrogen capacity materials towards the required range of operating temperature and pressure. The optimum scenario is to utilize the waste heat of the powerplant (e.g. fuel cell or internal combustion engine). For example, if H_2 could be released at acceptable rates at less than 80°C, the waste heat of the fuel cell could be utilized for endothermic desorption, i.e., avoiding the need to burn H_2 to generate the needed temperature. A useful alternative to the gravimetric versus volumetric capacity depiction is to show capacity as a function of temperature. Figure 4 shows the current status of materials development for the applied R&D Storage activity in terms of material-based capacity on a weight basis as a function of release or uptake temperature. The *system* level requirements for weight and temperatures are defined by the dashed lines (greater than 5.5 wt% and 7.5 wt% H_2 for the new 2015 and ultimate targets, respectively, and 0-100°C) to put the material-based capacities in perspective (i.e., ignoring system weight additions). The limitations in temperature are mainly due to thermodynamic properties (e.g., enthalpies or binding energies that are either too high or too low) and kinetics (e.g., hydrogen absorption or release rates are too slow at the required operating temperatures). It should also be noted that there is typically a range of temperature across which hydrogen is discharged (or charged). The values shown in Figure 4 have been updated for new candidates identified during FY 2009 and will be further modified by DOE as advancements are made in this rapidly progressing field.

Selected Examples of FY 2009 Accomplishments

Advanced Metal Hydrides

- High yields of gram quantities of pure alane (AlH_3) have been synthesized electrochemically bypassing expensive thermodynamics routes for its reversible regeneration and thereby making this hydride a more viable storage candidate. (R. Zidan, Savannah River National Laboratory member of the Metal Hydride CoE)
- A simple and energy-efficient single-stage procedure has been shown to rehydrogenate Ti-doped $LiAlH_4$ at ambient temperature and a moderate hydrogen pressure of 100 bars with a dimethyl ether (DME) solvent. (S. McGrady, University of New Brunswick, and C. Jensen, University of Hawaii, members of the Metal Hydride CoE) Preliminary thermodynamic analyses of the regeneration process from LiH , Al , and H_2 in the DME solvent showed the energy requirement to depend upon the molar ratio of DME to $LiAlH_4$ and to have the potential of achieving a 60 % well-to-tank (WTT) efficiency. (R. Ahluwalia, Argonne National Laboratory)
- A low temperature homogeneous organometallic approach has been used to incorporate about five times higher amounts of MgH_2 into carbon aerogels than was achieved via molten Mg metal. Both methods had similarly enhanced desorption kinetics compared to ball milled MgH_2 powders.

FIGURE 4. Hydrogen storage capacity for materials developed by the sub-program as a function of temperature. The open symbols represent new materials and/or data for FY 2009.

While LiBH_4 could be added to the aerogel after the MgH_2 , the subsequent desorption behavior indicated independent decomposition of the two hydrides presumably due to separate filling of the nano-pores rather than promoting the desired destabilization reactions. Variations in the filling and processing conditions are being explored to promote simultaneous occupancy of both hydrides into the pores. (C. Jensen, University of Hawaii, and J. Vajo, HRL, members of the Metal Hydride CoE)

- The aluminoborane compound $\text{AlB}_4\text{H}_{11}$ has been found to start releasing hydrogen at 125°C and can desorb 10.5 wt% H_2 by heating to 325°C. Substantial reversibility was also observed when TiCl_3 -catalyzed $\text{AlB}_4\text{H}_{11}$ was exposed to ~90 bar of H_2 at 200°C. This suggests that this material and related species may be attractive candidates for on-board hydrogen storage if the reaction temperatures can be lowered. (Collaborative effort of the Metal Hydride CoE partners Ohio State University, Oak Ridge National Laboratory, Jet Propulsion Laboratory, and California Institute of Technology)

Chemical Hydrogen Storage

- A detailed cost estimate for the regeneration of AB using the current thiol-based route indicated a cost of \$7-8/kg H₂ for large-scale production. Capital equipment recovery costs and cost of utilities were found to be the dominant components and were caused by the high volume process flows and multiple separations required for this pathway. This analysis suggested substantial cost reductions may be possible via alternative chemical reactions to lower processing and separation costs. (S. Linehan, Rohm & Hass Co., a member of the Chemical Hydrogen Storage CoE)
- A new approach using hydrazine to form the BH₃-containing species may regenerate decomposed AB in just one or two steps, which would be much simpler and reduce the mass of this reductant compared to the current baseline using Bu₄Sn-H as the reductant. The estimated thermodynamic

efficiencies are 83% and 65% for the hydrazine and $\text{Bu}_3\text{Sn-H}$ processes, respectively. (K. Ott, Los Alamos National Laboratory, member of the Chemical Hydrogen Storage CoE)

- Several approaches including scaffolds, nano-BN, methylcellulose, and metal substitutions (i.e., Li, Na) have been found to mitigate foaming during hydrogen desorption from AB. However, there are issues with excessive impurity levels (i.e., ammonia and borazine) that still need to be better controlled. (T. Autrey, Pacific Northwest National Laboratory, member of Chemical Hydrogen Storage CoE).
- Progress continued on increasing the hydrogen release rates from several ionic liquid/AB mixtures at temperatures below 120°C along with a total release that exceeded 10 wt%. A variety of catalysts were found to be effective. (L. Sneddon, University of Pennsylvania, and A. Burell, Los Alamos National Laboratory, members of the Chemical Hydrogen Storage, CoE).

Hydrogen Sorption

- Substantial efforts were devoted within the Hydrogen Sorption CoE towards gaining a better understanding of the mechanisms for the hydrogen spillover effects of metal particles on sorbent surfaces with the goal of improving both kinetics and storage capacity. Recent modeling studies have provided several new insights: (1) Hydrogen hopping between carbon surfaces is faster than diffusion on the surface; (2) Creation of holes in the valence band by either doping or defects lowers diffusion energy barriers to enable faster transport; (3) Non-precious metals components such as BC_3 can catalyze H_2 dissociation to serve as a less expensive spillover catalyst. (Hydrogen Sorption CoE members National Renewable Energy Laboratory, Air Products, and Rice University)
- A sample of Pd/Hg-doped carbon foam (CF) was reported to have an 8 wt% reversible hydrogen storage capacity at room temperature and 80 bar pressure from a collaborative assessment between the Southwest Research Institute® and the “Demokritos” Research Center in Greece. During the continuation of this joint study, the maximum room temperature capacity obtained on new preparations of the Pd/Hg-CF has not exceeded 2.1 wt% at 88 bar, which might be attributed to different segregation of the catalyst during processing. On the other hand, laser induced chemical desorption mass spectrometry measurements have indicated hydrogen can bind to oxygen-bearing carbons leading to water evolution during desorption. Further studies are underway to resolve this issue. (M. Miller, Southwest Research Institute®).
- Layered carbon structures are being explored as one means to increase the hydrogen sorption enthalpy (ΔH) from the nominal range of 4-6 kJ/mole for most carbon sorbents (i.e., activated AX-21 carbon and MOF-155) to larger values for increased adsorption above liquid nitrogen temperature. One clear example of this effect occurs with the compound CsC_{24} where $\Delta H = 13$ kJ/mole for a broad range of hydrogen content such that this material retained ~50 % of its 77 K capacity, which is 1.8 wt%, at 195 K. (C. Ahn, California Institute of Technology, member of the Hydrogen Sorption CoE)
- Catenation (i.e., intergrowth of two or more identical frameworks) in porous MOFs has led to a 41% improvement of apparent Langmuir surface area (3,800 m^2/g for PCN-6 vs. 2,700 m^2/g for PCN-6'), a 29% increase in excess gravimetric hydrogen uptake (1.74 wt% for PCN-6 vs. 1.35 wt% for PCN-6') at 77 K/760 torr, and a 263% increase in volumetric hydrogen uptake (9.19 kg/m^3 for PCN-6 vs. 3.49 kg/m^3 for PCN-6') in the catenation isomer pair of PCN-6/PCN-6'. In addition, increased isosteric heats of adsorption were observed with ΔH reaching 12.5 kJ/mole in some cases. (H. Zhou, Texas A&M University, member of the Hydrogen Sorption Center)

Compressed and Cryogenic Tanks

- Updated projections of the performance levels and costs for high-volume (i.e., 500,000 units/yr) production levels have been made for composite tank systems with 350 bar and 700 bar gas storage at ambient temperature. These analyses included revised designs of the tank shape, changes in materials properties, and modified pressure safety factors. The gravimetric capacities for the 350 bar and 700 bar tanks rose to 5.9 wt% and 4.7 wt%, respectively, which are above or near the new 2015 target of 5.5 wt%. Although their volumetric capacities increased to 17.5 $\text{g-H}_2/\text{L}$ and 25 $\text{g-H}_2/\text{L}$, they are still much lower than the 2015 target of 40 $\text{g-H}_2/\text{L}$. The costs of these systems

decreased to \$15.5 kWh (350 bar) and \$23.1 kWh (700 bar), which are 9-13% less than prior estimates since less carbon fiber material is required for the reduced pressure safety factors. These volumetric and costs results emphasize the need for low-pressure materials-based storage systems if targets are to be met. (TIAX, LLC and Argonne National Laboratory)

- A third generation (Gen 3) cryogenic vessel has been designed and fabricated for cryo-compressed hydrogen storage. Initial tests of the Gen 3 tank verified system capacities (7.4 wt% hydrogen and 45 g-H₂/L, exceeding the new 2015 targets); and indicated promising dormancy properties and costs relative to conventional liquid hydrogen tanks. (Lawrence Livermore National Laboratory)

Testing, Materials Properties and Analysis Cross-Cutting

- The document “*Recommended Best Practices for the Characterization of Storage Properties of Hydrogen Storage Materials*” December, 2008, was completed by K.J. Gross and K.R. Carrington and is now available. (http://www1.eere.energy.gov/hydrogenandfuelcells/pdfs/bestpractices_h2_storage_materials.pdf) This document provides comprehensive assessments of the various volumetric and gravimetric methods that are most commonly employed to measure hydrogen storage capacities and kinetics. It addresses both the fundamentals of these techniques and issues that can arise when they are implemented for most hydrogen storage media. Hence it serves as a valuable resource for novice and experienced researchers in the hydrogen storage R&D community.
- Comprehensive analyses of performance parameters and the costs for large-scale production (i.e., 500,000 units/yr) were performed or updated on several on-board physical and chemical hydrogen storage systems. However, costs for all systems analyzed to date still greatly exceed the DOE 2010 target of \$4/kWhr reflecting the need for more innovations. (TIAX, LLC and Argonne National Laboratory)
- The WTT efficiencies for refueling several hydrogen storage systems were predicted for comparison to the DOE target of at least 60%. Estimates included: AB (~37% for the baseline regeneration process), liquid hydrogen (~40%), alane slurry (~40-55%, depending on low-grade waste heat available); the liquid carrier N-ethylcarbazole (~60%). Further analyses are in progress on alternative regeneration processes with lower energy requirements that should improve the WTT values for ammonia borane and alane. (Argonne National Laboratory)
- Three independent but coordinated projects are assessing the chemical reactivity and safety aspects of representative hydrogen storage materials (i.e., AlH₃, NaAlH₄, 2LiBH₄/MgH₂, NH₃BH₃, and the activated carbon AX-21), which correspond to the diverse range of candidates for future storage systems. Progress made during the past year encompasses qualitative and quantitative risk analyses for environmental exposures and potential accident scenarios; testing of materials properties (e.g., dust cloud flammability and pyrophoricity, reactivity during air and/or water exposures, and identification of product species formed); and development of possible mitigation methods such as fail-safe foams or organic liners that restrict air exposures in an accident. These studies have included the active participation by research groups in Canada, Germany, and Japan as part of international cooperative programs. (Savannah River National Laboratory, Sandia National Laboratory, United Technologies Research Center)

FY 2010 Plans

The technology portfolio for Hydrogen Storage emphasizes materials R&D to meet system targets for on-board applications with a focus on alternatives to high-pressure or cryogenic tanks. The three Materials CoEs will end in FY 2010 according to their five-year plans. Each center will thoroughly document and report their findings and conclusions. In particular, the performance capabilities and limitations of the various types of storage materials will be documented in order to facilitate development of viable hydrogen storage systems for vehicle and early market applications. This information will be accessible to researchers, the fuel cell industry, and the general public.

The sub-program will focus on improving material volumetric capacity, hydrogen uptake and discharge kinetics, overall system efficiency, durability and life cycle cost. The storage R&D portfolio will be adjusted to include the specification and development of advanced technologies for stationary,

portable, and back-up fuel cell power systems. The coordination with basic science, including theory, characterization and novel concepts, will continue during FY 2010.

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IV.A.1a DOE Metal Hydride Center of Excellence

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- National Institute of Standards and Technology (NIST)
- Oak Ridge National Laboratory (ORNL)
- Ohio State University (OSU)
- Sandia National Laboratories (SNL)
- Savannah River National Laboratory (SRNL)
- Stanford University (Stanford)
- United Technologies Research Center (UTRC)
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Start Date: March 2005
Projected End Date: October 2010

Introduction

The DOE Metal Hydride Center of Excellence (MHCoE) consists of 10 universities (Caltech, Georgia Institute of Technology, Stanford, University of Hawaii, University of Illinois at Urbana-Champaign, University of Nevada, Reno, University of New Brunswick, University of Pittsburgh, Ohio State University and the University of Utah), six national laboratories (Brookhaven National Laboratory, Jet Propulsion Laboratory, National Institute of Standards and Technology, Oak Ridge National Laboratory, Sandia National Laboratories, and Savannah River National Laboratory) as well as two industrial partners (HRL Laboratories, United Technologies Research Center). SNL is the lead laboratory, providing technical leadership for the center and a center structure to guide the overall technical program and advise the DOE.

The purpose of the MHCoE is to develop hydrogen storage materials and engineering properties that allow the use of these materials in a way that satisfies the FreedomCAR Program system requirements for automotive hydrogen storage. In an overall sense, our Center is a multidisciplinary and collaborative effort with the collaborations divided into three broad areas: mechanisms and modeling (which provide a theoretically driven basis for pursuing new materials), materials development (in which new materials are synthesized and characterized) and system design and engineering (which allow these new materials to be realized as practical automotive hydrogen storage systems). Driving all of this work are the hydrogen storage system specifications outlined by the FreedomCAR Program for 2010 and 2015.

The organization of the MHCoE during the past year is shown in Figure 1.

During the past year, the technical work was divided into four project areas. The purpose of the project areas is to organize the MHCoE technical work along appropriate and flexible technical lines.

Project A (Destabilized Hydrides) was led by Prof. Bruce Clemens, Stanford University. The objective of this project is to develop strategies for reducing hydrogen storage thermal requirements and improve kinetics by destabilizing metal hydrides systems. The technical approach is to alter the thermodynamics of the storage system by destabilizing the metal hydride through alloying, thereby reducing the energy needed to liberate hydrogen from the material, and reducing the desorption temperature. Project A also aims to enhance kinetics by evaluating nanoengineering approaches to minimizing the required hydrogen diffusion distance by decreasing particle size and creating nano-engineered scaffolds.

Project B (Complex Anionic Materials) is led by Prof. Craig Jensen (University of Hawaii). The objective here is to predict and synthesize highly promising new anionic hydride materials. The technical approach involves using theory and chemical intuition to select promising target complex hydrides. Candidate materials are then synthesized by a variety of techniques, followed by extensive structural and hydrogen sorption characterization. A particular focus in Fiscal Year 2009 has been on borohydride materials.

Project C (Amides/Imides Storage Materials) is led by Prof. Zak Fang of the University of Utah. The objective of Project C is to assess the viability of amides and imides (organic materials containing -NH_2 and -NH moieties, respectively) for onboard hydrogen storage. The technical approach is to reduce thermal

FIGURE 1. Organization of the MHCoe, with Project Areas

requirements of these materials by alloying, understand and elucidate the chemical pathways by which these materials release and absorb hydrogen, and determine the initial engineering issues (thermal cycling) of these materials.

Project D (Alane, AlH_3) is headed by Dr. Jim Wegrzyn of Brookhaven National Laboratory. The objective of Project D is to understand the sorption and regeneration properties of alane (AlH_3) for hydrogen storage. The technical approach has been to synthesize the various structural forms of AlH_3 , and characterize the structure and hydrogen sorption properties of these forms. The emphasis in FY 2009 has been on regenerating AlH_3 from Al, using solution-based, electrochemical, and supercritical fluid methods.

In addition to these formal “Projects”, we have three working subgroups in the MHCoe. The MHCoe Theory Group (TG) is coordinated by Dr. Mark Allendorf (SNL), and makes use of first-principles methods to predict new materials and their thermodynamic properties, and suggests new directions for experimentalists and interpretation of their results. The TG consists of researchers at five institutions: SNL, Pitt/GT, UIUC, NIST and UTRC. To make maximum use of the different areas of expertise, joint TG efforts are guided by SNL not only in terms of technical direction, but also to ensure that TG efforts are complementary and have an effective synergism with experimentalists.

A second working group in the MHCoe is the “Additive Screening Group”. This group, coordinated by Dr. Eric Majzoub (University of Missouri-St. Louis, on leave from SNL) examines the effects of catalysts and other additives on the kinetic and thermodynamic properties of metal hydrides. The group makes use of MHCoe kinetics stations, Sieverts apparatus, and

pressure-concentration-temperature instruments to screen many catalysts and additives for their effects on hydrogen desorption temperature, kinetics of adsorption/desorption, and material reversibility. This group involves almost all experimentalists in the MHCoe.

The third working group is the “Amine-Boro Complex” working group, led by Prof. J.-C. Zhao of Ohio State University. Recently, Prof. Zhao has shown that ammonia can complex with $\text{Mg}(\text{BH}_4)_2$ to produce an amine-boro complex that releases hydrogen at substantially lower temperature than $\text{Mg}(\text{BH}_4)_2$ alone. This finding has spawned a larger effort in such materials within the MHCoe, activity which is coordinated by the Amine-Boro Complex working group.

MHCoe Objectives

Our highest level objective is to:

- Develop new reversible hydrogen storage materials to meet or exceed DOE/FreedomCAR 2010 and 2015 system goals.

Technical Barriers

The MHCoe tackles well-defined technical barriers associated with reversible solid-state hydrogen storage systems in which hydrogen is desorbed and re-absorbed on board the vehicle. These barriers are reproduced below from the Onboard Hydrogen Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- A. Cost (Low-cost materials and components for hydrogen storage systems are needed, as well as low-cost, high-volume manufacturing methods.)
- B. Weight and Volume (Materials and components are needed that allow compact, lightweight, hydrogen storage systems while enabling greater than 300-mile range in all light duty vehicle platforms. Reducing weight and volume of thermal management components is required.)
- C. Efficiency (The energy required to get hydrogen in and out of the material is an issue for reversible solid-state materials. Thermal management for charging and releasing hydrogen from the storage system needs to be optimized to increase overall efficiency.)
- D. Durability (Materials and components are needed that allow hydrogen storage systems a lifetime of 1,500 cycles with tolerance to fuel contaminants.)
- E. Refueling Time (There is a need to develop hydrogen storage systems for the refueling times of less than three minutes for 5 kg of hydrogen, over the lifetime of the system. Thermal management during refueling is a critical issue that must be addressed.)
- G. System Life Cycle Assessments (Assessments of the full lifecycle, costs, efficiency, and environmental impact for hydrogen storage systems are lacking.)

Technical Targets Addressed by MHCoe

While all of the targets detailed in the DOE Multi-Year Research, Development and Demonstration Plan will be addressed, our main emphasis initially focuses on the DOE specifications for system specific energy density (2.0 kWh/kg [2010], 3.0 kWh/kg [2015]) and system volumetric energy density (1.5 kWh/L [2010], 2.7 kWh/L [2015]). These targets, in an overall way, drive our “down-select” process for materials. The procedure used to select materials for further study has been documented in the following report submitted to DOE:

“Materials Go/No-Go Decisions Made Within the DOE Metal Hydride Center of Excellence (MHCoe),” L.E. Klebanoff, October 5, 2007, Summary report posted on DOE Hydrogen Storage Website: http://www1.eere.energy.gov/hydrogenandfuelcells/hydrogen_publications.html#h2_storage

Selected MHCoe Technical Highlights for FY 2009

During the past year, the MHCoe has published 61 papers (26 of these collaborations between MHCoe partners) in the leading journals of chemistry, physics, materials science and crystallography. In addition, MHCoe scientists delivered 71 talks at national and international meetings, and filed five patent applications.

MHCoe scientists are professional leaders in the general field of hydrogen interactions with materials.

Below we present selected highlights from the MHCoe technical work over the period 3/2008-6/2009. Please consult the partner's individual annual report (following) for more details.

MHCoe Technical Highlights

1. Developed capability to include important gas-phase species in phase equilibrium calculations for H₂ release from LiNH₂, LiBH₄/C (SNL, Pitt, GT).
2. Synthesized pure LiMgN, found ΔH desorption to be ~20–30 kJ/mole H₂, in overall agreement with MHCoe theory (Utah).
3. Found that slurry AlH₃ H₂ release rates are greater than for AlH₃ alone (BNL).
4. Achieved full destabilized system (LiBH₄/MgH₂) in C-aerogel (HRL).
5. Achieved breakthrough in electrochemical regeneration of AlH₃, producing gram quantities of high purity AlH₃ with high H₂ content (SRNL).
6. Found that discharged LiAlH₄ (LiH, Al[Ti]) can be conveniently regenerated at room temperature in 100 bar of Me₂O/H₂ (UNB, UH).
7. Demonstrated high loading of NaTi(BH₄)₄ in SiO₂ aerogel, with the aerogel improving hydride stability (UTRC, Albemarle).
8. Found a procedure that allows Mg(BH₄)₂ to reverse at 700 bar H₂, 350°C (UH, SNL).
9. Advanced our understanding of MxB₁₂H₁₂ (M = Li, Na, Ca, Mg) compounds, which are important intermediates during H₂ release from borohydrides (NIST, OSU, SNL, Caltech/JPL).
10. Discovered a liquid phase organometallic route to incorporating MgH₂ into a C-aerogel, and observed a concomitant 60x improvement in H₂ desorption rate (UH, HRL).
11. Successfully synthesized AlB₄H₁₁, found it to release ~8 wt% hydrogen at 250°C, and observed partial reversibility under mild conditions (200°C, 5 hours at 90 bar H₂) (OSU, ORNL, Caltech, JPL).
12. Developed a quartz-crystal microbalance chamber that is able to characterize P_{eq} in very thin films exposed to hydrogen. Facility will allow a determination if size reduction influences thermodynamics in thin films and islands (Stanford).
13. Combined state-of-the-art scanning transmission electron microscopy and reaction theory to reveal Ca(BH₄)₂ reaction mechanism (UIUC).
14. Successfully determined the effect of various gaseous impurities (O₂, CO, H₂O, CH₄, NH₃) in ultra-high purity hydrogen on the cycling behavior of LiNH₂. The study simulates the filling of hydrogen in a

future hydrogen gas station where these gases are expected to have ppm levels of impurities (UNR).

Awards and Honors

1. Jay Keller, the MHCoE Deputy Director and Sandia Hydrogen Program Manager, received the 2009 “DOE Hydrogen Program Special Recognition Award” for years of outstanding contributions to the DOE Hydrogen Program.
2. Jason Graetz, Brookhaven National Laboratory, received a 2009 DOE Presidential Early Career Award for Scientists and Engineers (PECASE). The PECASE award is the highest honor bestowed by the United States government on outstanding scientists and engineers beginning their independent careers.
3. Ian Robertson, University of Illinois at Urbana Champaign, was elected a “Fellow of the Society” by the Board of Trustees of ASM International. Dr. Robertson was cited “for pioneering studies using time-resolved transmission electron microscopy to study metal deformation processes in aggressive environments, as well as production and annihilation of defects.”
4. Don Anton, Savannah River National Lab, was also elected a “Fellow of the Society” by the Board of Trustees of ASM International. Dr. Anton was cited for “significant and sustained contributions to materials science and technology in the areas of fatigue, superalloys, intermetallics and hydrogen storage materials and systems.”

IV.A.1b Thermodynamically Tuned Nanophase Materials for Reversible Hydrogen Storage: Structure and Kinetics of Nanoparticle and Model System Materials

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Contract Number: DE-FC36-05GO15061

Project Start Date: January 1, 2005
Project End Date: February 28, 2010

Objectives

Develop fundamental understanding of metal hydride reaction kinetics:

- Kinetics limit practicality and reversibility of many promising metal hydride material systems:
 - Mg, Mg₂Si, Li₄Si, NaAlH₄, LiBH₄+MgH₂, etc.
 - Initial work on Mg₂Si showed that kinetic issues prevent system from achieving reversibility.
- Catalyst additions have shown some success in improving kinetics for some systems (i.e. Ti in NaAlH₄), but little is known about the nature of these effects.
- Little is known about the kinetic mechanisms present in these systems, and in order to improve the kinetics for any of these metal hydride systems a sound understanding must be developed.

Develop understanding of metal hydride nanostructure thermodynamics:

- Many systems suffer from inappropriate thermodynamics (equilibrium pressure):
 - Mg, Al

- Continuum modeling suggests that reaction thermodynamics should be modified by reducing particle size to the nanometer regime.

Develop understanding of metal hydride structures during phase change:

- Material structure can play important role in reaction kinetics, especially during solid state phase transformations such as those in metal hydride reactions.
- Understanding the interplay between material structure and reaction kinetics may provide insight on how to successfully engineer new materials with improved kinetics and storage properties.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) System Weight and Volume
- (D) Durability/Operability
- (E) Charging/Discharging Rates
- (P) Lack of Understanding of Hydrogen Physisorption and Chemisorption

Technical Targets

Our project conducts fundamental research of metal hydride storage material reaction kinetics and thermodynamics, examining the effects of material structure and particle size on each using thin films and vapor deposition techniques to probe the effects in a controlled and quantitative manner. The research addresses the following DOE 2010 hydrogen storage technical targets:

- Gravimetric Capacity: 0.045 kg H₂/kg
- Min/Max Delivery Temperature: -40/85°C
- System Fill Time: 4.2 min
- Minimum Full Flow Rate: 0.02 (g/s)/kW

Accomplishments

- Reaction depth into Mg₂Si <1 nm, making system impractical for reversible storage.

- Hydride growth kinetic experiments support moving planar interface model, <60 nm of reaction controlled growth from data – anything thicker suffers from diffusion limited growth (slower).
- Quartz crystal microbalance (QCM) chamber able to detect P_{eq} in very thin Mg layers, no size vs. P_{eq} dependence seen yet.
- Addition of 5% Ti in Mg gives ~10x increase in P_{eq} , verification needed with further study.
- Mg/Al kinetic study underway using multilayer film/X-ray diffraction (XRD) approach successfully used with Mg_2Si .
- Neutron reflectivity with the National Institute of Standards and Technology (NIST) underway to measure reaction depth and microstructure in epitaxial Mg films.

Introduction

The mechanism and kinetics of the metal/metal hydride transformation in metal hydride hydrogen storage materials plays a crucial role in determining whether a material meets the DOE on-board storage targets for 2010 and 2015. A fundamental understanding of these issues provides valuable insight into the ways in which various material systems can be engineered in order to meet specific material targets. Additionally, as the ability to engineer materials on the nano-scale emerges, new routes to tailoring specific material properties become possible. Specifically, by reducing the dimensions of metal hydride storage materials you can alter properties such as the hydrogen vapor pressure and storage capacity.

We extensively investigated reduced dimension metal hydride material systems and their hydrogen charging and discharging properties. We determined kinetic behavior and transformation mechanisms for magnesium-based thin film material systems using in situ hydriding and dehydriding with detailed XRD to examine the effects of material cycling. We also investigated the effects of reduced dimensionality on destabilized material systems such as Mg_2Si . Additionally, we modeled the effects of reducing dimensions of hydrogen storage materials to the nano-scale (i.e. nanoparticles), revealing the possibility of drastically altered hydrogen storage properties in metal hydride nanoparticles, and constructed an analysis chamber to probe the differences in hydrogen storage properties (both thermodynamic and kinetic) between bulk and nanoscale systems. Furthermore, we investigated kinetic and thermodynamic behaviors in the Mg/Ti and Mg/Al material systems.

Approach

In order to determine ways to engineer material systems to meet the DOE on-board storage targets for 2010 and 2015 we use a combination of thermodynamic modeling efforts combined with nanoscale material synthesis and various characterization techniques to gain a better understanding of the underlying kinetic mechanisms present in the metal hydride phase transformations. We make extensive use of XRD techniques, using both in-house facilities and facilities at the Stanford Synchrotron Radiation Lightsource, to characterize the structural changes of material systems as they undergo phase changes during hydrogen absorption and desorption. We can then correlate this structural information with kinetic data about the absorption and desorption rates to relate the structure of materials to their kinetic behavior. Additionally, we employ the use of a QCM apparatus to quantify the hydrogen uptake in extremely small sample sizes, allowing us to determine reaction thermodynamics and kinetics for thin film and nanoparticle samples. Finally, the modeling efforts provide insight on where future experiments should focus and help to explain behaviors seen in experimentally synthesized samples prepared using physical vapor deposition techniques.

Results

Over the last year, we made progress in several areas of our research and we continued utilizing our thin film deposition and analysis capabilities to investigate the fundamental kinetic mechanisms present in metal/metal hydride phase change reactions as well as the effect of particle size on both reaction kinetics and thermodynamics.

In our previous work investigating the reversibility of the Mg_2Si system, we saw very little evidence for the formation of the hydride phase when starting from Mg_2Si and hydrogen. However, when we processed the data from that study we noticed a systematic trend in the XRD data relating the amount of Mg_2Si material remaining to the thickness of the original Mg_2Si layer in multilayer films containing alternating layers of Mg and Mg_2Si . If we assume the hydriding reaction proceeds from the edge of the Mg_2Si layer inwards from both sides, then we can relate the fraction of Mg_2Si material remaining after hydrogenation, f , to the reaction depth, d , through the equation $f = 1 - 2d/l$, where l is the initial Mg_2Si layer thickness. Then, through careful XRD measurements of the Mg_2Si peak intensities before and after exposure to hydrogen, we can measure the fraction of Mg_2Si remaining and plot it versus the inverse layer thickness. Then, by fitting a line to the data we can extract d , the reaction depth into the Mg_2Si layer. Figure 1 shows the data from our experiment along with a linear fit constrained to go through 1 for

FIGURE 1. $\text{Mg}_2\text{Si}(111)$ XRD peak intensity ratios (after hydrogen annealing/before annealing) vs. reciprocal Mg_2Si layer thickness with a linear fit to the data constrained to go through 1 for infinite layer thickness.

infinitely thick ($1/l = 0$) Mg_2Si layers. The linear fit gives a reaction depth into the Mg_2Si layer of less than 0.5 nm. This means that, in order to achieve total hydrogenation, one would need stable Mg_2Si particle sizes below 1 nm. To put this in perspective, this represents a particle less than two Mg_2Si unit cells across. Particles of this size are extremely difficult to synthesize and rarely show properties concurrent with their bulk counterparts. These results indicate that the Mg_2Si system is not limited by hydrogen diffusion through Mg_2Si or nucleation of the MgH_2 phase, but rather by the transport of Mg and Si during phase segregation into separate MgH_2 and Si phases. In other words, the host atoms diffuse much slower than the hydrogen atoms in this system, leading to limited reversibility. Despite the promising thermodynamics of this system, kinetic limitations prevent it from performing as a practical material on even a modest scale.

Building on the success of the experiments on the Mg_2Si system, we applied our thin film platform approach to the Mg/Al system. This system exhibits similar kinetic problems to Mg_2Si where the hydride phase ($\text{Mg}(\text{AlH}_4)_2$) fails to form from the constituent phases MgH_2 , Al and H_2 . In order to investigate this, we deposited several multilayer samples containing alternating Mg and Al layers with Pd capping layers, varying the Al layer thickness in each film. The multilayer films deposited as superlattices due to similarities in the lattice parameters for Mg and Al. However, XRD analysis shows evidence for layer intermixing between the Mg and Al at room temperature over the course of a few days. After exposure to 1 bar

H_2 gas at 110°C for 10-20 hours, some XRD spectra showed no change relative to immediately before the anneal while others showed evidence for intermetallic phase formation, such as $\text{Mg}_{17}\text{Al}_{12}$. This experiment reveals that the films do not readily react with hydrogen as none of the films showed evidence for MgH_2 formation. The films seem to form Mg/Al alloy phases and these intermetallic phases, or the Al itself seem to block the hydrogen from entering the structure or they simply do not form a hydride phase. In order to determine the origin of these finding, we plan to study additional film structures where an Al layer of varying thickness lies between a single Mg layer and the Pd capping layer. These films will help determine the ability of hydrogen to diffuse through the film structure. The preliminary experiments seem to indicate that, in this system, hydrogen diffuses slowly while the host atoms diffuse fairly easily within each other, leading to alloy formation without evidence for any hydride phase formation.

We also made significant progress in our ongoing effort to develop a detailed model of the kinetic processes present in metal hydride phase transitions by utilizing highly controlled epitaxial Mg thin films. Our previous results showed strong evidence for hydride phase formation by a moving planar interface growth mechanism similar to the growth of an oxide layer on silicon first outlined by Deal and Grove [1]. However, this model applies only to semi-infinite slabs of Mg where the hydride layer may continue to grow forever. To accommodate our thin film samples, we modified this model by implementing a cutoff where the derivative of the interface position decreases linearly to zero over a width in time that corresponds to when the leading and trailing edges of the interface (due to roughness) reach the substrate. The in situ XRD data in Figure 2 shows integrated intensity versus time for the Mg(002) peak of 2,000 Å, 4,000 Å and 8,000 Å thick epitaxial Mg films grown on (001) Al_2O_3 with 250 Å thick Pd capping layers. The solid lines in Figure 2 represent fits to the function obtained from the diffusional model containing the cutoff described above to accommodate the finite thickness of the films. The good agreement between the data and model functions provides strong evidence for hydride growth through a moving planar interface from the top of the film downward. Figure 3 shows the data for the 4,000 Å and 2,000 Å thick films from Figure 2 plotted on a log-log scale with the data re-scaled to start at the graph origin in order to reveal the different regimes of the reaction. The faster linear regime (reaction limited) for both films is confined to Mg thicknesses below 60 nm. Beyond 60 nm the reaction transitions to the slower $t^{1/2}$ (diffusion limited) regime until the entire film transforms to the hydride phase. Extrapolating the $t^{1/2}$ trend to longer times shows that to transform a 1 μm thick film should take ~50 hours, consistent with literature reports. This analysis indicates

FIGURE 2. Mg(002) peak intensities vs. time for 2,000 Å, 4,000 Å and 8,000 Å thick films (symbols) showing good agreement to a fit of the function for moving interface hydride growth developed in this report.

FIGURE 3. Log-log plot of the data for the 2,000 Å and 4,000 Å data shown in Figure 2 renormalized to zero intensity at zero time, showing a transition between the “linear” and “square root” growth regimes at a hydride thickness of ~ 600 Å. The data shows a time to hydride a $1\ \mu\text{m}$ film of ~ 50 hours.

that, to retain the faster linear reaction rates, material structures should have critical dimensions less than 120 nm (twice 60 nm). It also provides motivation for future studies to provide more details about the kinetic mechanisms present in the metal/hydride phase transition in this technologically important material.

We made progress using our QCM hydrogen chamber to analyze several different metal hydride materials. Our previous work using continuum modeling to analyze the effect of reduced dimensionality on metal hydride thermodynamics indicated an increase in the equilibrium pressure for magnesium particles with critical dimensions below ~ 10 nm. To investigate this we examined a thin film sample consisting of alternating layers of Mg and Pd, looking for equilibrium

FIGURE 4. van't Hoff plot showing the natural log of the equilibrium pressure vs. reciprocal temperature for several samples measured with the QCM hydrogen pressure chamber. The 400 nm thick Mg film and the 5 nm thick Mg/Pd bilayer films both show equilibrium pressures consistent with bulk Mg. The Mg + 10 wt% Ti film shows equilibrium pressure $\sim 10\times$ that of bulk Mg and the Mg thin film samples.

pressure in the QCM chamber by watching for the pressure where mass uptake ceased as we stepped from above the equilibrium pressure to successively lower pressures. As shown in Figure 4, the equilibrium pressure for a 400 nm thick Mg film matches well with that reported in the literature² for thicker Mg films. A multilayer film with alternating 5 nm thick Mg layers and 10 nm Pd layers shows a preliminary equilibrium pressure measurement consistent with the measurements from the thicker film, indicating that the size effect predicted is much smaller in reality, or is significantly modified by the presence of the Pd layers. However, the measurement demonstrates the sensitivity of the QCM chamber technique. In another sample consisting of 400 nm of Mg + 10 wt% Ti deposited as a metastable solid solution capped with 25 nm of Pd on a QCM crystal we observe an equilibrium pressure increase of $\sim 10\times$ compared to thicker Mg films, as shown in Figure 4. The extracted enthalpy of reaction according to our data (-55 kJ/mol) matches well with calculated values from literature (-52 kJ/mol) [3] and our equilibrium pressure measurements match well with other literature reports for similar systems [4,5]. Further work may shed light on the role of Ti concentration level on the equilibrium pressure in this system as well as the kinetic mechanisms present in the transformation.

Finally, we continued our collaboration with the team at NIST to examine the microstructural development of epitaxial Mg films when exposed to hydrogen using neutron reflectivity. We are set to perform in situ reflectivity experiments on a monolithic 1000 Å Mg film grown on (001) oriented Al_2O_3 and capped with 250 Å Pd. By taking measurements at different stages of hydrogenation and dehydrogenation we can track the motion of the Mg/MgH₂ interface and

determine the configuration of the film as the hydride phase forms. Preliminary modeling indicates that we should be able to resolve these features fairly reliably.

Conclusions and Future Directions

Conclusions

- Reaction depth into Mg_2Si < 1 nm, making system impractical for reversible storage.
- Hydride growth kinetic experiments support moving planar interface model, < 60 nm of reaction controlled growth from data – anything thicker suffers from diffusion limited growth (slower).
- QCM chamber able to detect P_{eq} in very thin Mg layers, no size vs P_{eq} dependence seen yet.
- Addition of 5% Ti in Mg gives $\sim 10\times$ increase in P_{eq} , verification needed with further study.
- Mg/Al kinetic study underway using multilayer film/XRD approach successfully used with Mg_2Si .
- Neutron reflectivity with NIST underway to measure reaction depth and microstructure in epitaxial Mg films.

Future Directions

- Continue data collection and analysis with QCM chamber:
 - Find and exploit the limits of hydrogen uptake sensitivity for the instrument.
 - Attempt to confirm theoretical predictions about the change in equilibrium pressure as particle size is reduced.
 - Examine kinetics and thermodynamics for thin film and nanoparticle samples.
- Finish Mg/Al study:
 - New film architectures.
 - Higher pressure H_2 anneals.
 - Faster turnaround to prevent intermixing.
- Finalize nanoscale Mg study:
 - Thinner Mg layers on QCM.
 - Careful measurements on existing samples.

- Further develop MgH_2 kinetic model:
 - Develop general model to describe reverse reaction and phase growth with cycling.
- Continue/finalize Mg/Ti study:
 - Examine different Ti concentrations to look for P_{eq} differences and trends.
 - Examine cycling behavior of Ti-doped Mg films compared to pure Mg.
- Continue with neutron reflectivity study on Mg/MgH_2 thin films with NIST:
 - Determine more specifics of reaction kinetics.
 - Interface motion/roughness/sharpness/etc.
 - Utilize new in situ hydrogen loading chamber at NIST.
 - Develop new models to describe data and incorporate findings into MgH_2 growth model.

FY 2009 Publications/Presentations

1. “Nanostructured Materials for Hydrogen Storage,” Combined Materials Science and Engineering Physics Departmental Colloquium, Colorado School of Mines, March 2008.
2. “Quantitative quartz crystal microbalance studies of equilibrium pressures in thin film and nanoparticle metal hydrides,” Material Research Society Spring Meeting, San Francisco, CA, March 2008.
3. “Kinetic limitations of the Mg_2Si system for reversible hydrogen storage”, *Nanotechnology* vol. 20 p. 204017.

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IV.A.1c Development of Metal Hydrides at Sandia National Laboratories

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University of Missouri – St. Louis, St. Louis, MO

Project Start Date: January 2005

Project End Date: October 2010

Objectives

- Discover and develop new materials with potential to meet the DOE 2010 targets for system weight percent and charge/discharge rates.
- Theoretically predict and synthesize new materials that release hydrogen with favorable thermodynamics.
- Screen catalysts and additives for their efficacy in improving the kinetic performance of metal hydrides.
- Provide theoretical understanding on metal hydride kinetic and regeneration problems.

Technical Barriers

This project addresses the following technical barriers from the Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) System Weight and Volume
- (C) Efficiency
- (E) Charge/Discharging Rates
- (J) Thermal Management

Technical Targets

Work is progressing on improving the reversibility of metal hydrides, predicting and synthesizing new metal hydrides with high hydrogen capacity and good thermodynamics, and understanding metal hydride kinetic and regeneration issues. The targets being addressed include:

- System Gravimetric Capacity: 0.06 kgH₂/kg system
- System Volumetric Capacity: 0.045kgH₂/L system
- Fill Time (for 5 kg): 3 minutes

Accomplishments

- Completed a comprehensive prototype electrostatic ground state (PEGS) study of the polymorphs of Ca(BH₄)₂, validated with experimental findings.
- Measured the enthalpy of desorption of Ca(BH₄)₂, found it to be 60-100 kJ/mole H₂. This enthalpy is too large for Ca(BH₄)₂ to be considered a viable hydrogen storage material.
- Experimentally synthesized a variety of metal-B₁₂H₁₂ salts, thereby gaining understanding of their chemistry and role as intermediates in borohydride-based hydrogen storage.
- Found that CaB₁₂H₁₂ cannot be readily hydrogenated, explaining in part the poor cycling characteristics of Ca(BH₄)₂.
- Using simultaneous thermogravimetric modulated beam mass spectrometry (STMBMS), found that Ca(BH₄)₂ releases substantial BH₃ along with H₂ when heated.
- “Downselected” Ca(BH₄)₂, removing it from further study as a viable hydrogen storage material.
- Completed theoretical studies of the reaction pathways and thermodynamics of hydrogen desorption from Mg(BH₄)₂ and Ca(BH₄)₂.
- Developed a method to dope MgB₂ with carbon, thereby opening up a study of the effects of C on Mg(BH₄)₂ hydrogen release.
- Initiated a study of the properties of Ti(BH₄)₃, opening up future studies of mixtures of borohydrides with Ti(BH₄)₃.
- Synthesized ammonia additives of mixed metal borohydrides, found them to behave very differently from the ammonia adduct of magnesium borohydride.
- Initiated studies of mixtures of borohydrides and amides, found reduced thermal requirements for some compounds.
- Initiated studies of P-based hydrogen storage materials. Found that Na[PH₂(BH₃)₂] could be synthesized, and the compound releases hydrogen at ~150°C.
- Developed a route to incorporating Ca(BH₄)₂ into C-aerogel with 50% loading, completing our work on the nanoframeworks project with United Technologies Research Center (UTRC).
- Completed phase equilibrium theoretical studies of the LiNH₂, LiNH₂ + LiH and LiBH₄ + C systems.

Found that gas phase species other than H_2 are important for determining reaction pathways and thermodynamics.

- Quantum chemical calculations show that the AlH_3 complex with triethylamine is the least stable of the amines and thus most easily decomposed to release pure AlH_3 . Of the ethers, $AlH_3O(C_2H_5)_2$ has the smallest complexation energy.

Introduction

There are currently no materials that fully meet the DOE hydrogen storage performance targets. In order to address this problem, we at Sandia National Laboratories (SNL) have undertaken the prediction, synthesis and characterization of new high-hydrogen content complex metal hydrides for use as reversible hydrogen sorption materials. In addition, we have further modified these hydrides through catalyst doping and cation substitution in order to improve their reversibility and sorption properties. Computational modeling has assisted in directing these efforts, as well as understanding kinetic and regeneration issues for metal hydrides. We provide technical leadership and collaborate extensively with our partners in the Metal Hydride Center of Excellence (MHCoe).

Approach

We are using an integrated theory/experiment approach to tackle the most challenging aspects of hydrogen storage in metal hydrides. Theoretical calculations are used to guide the search for better materials by (i) identifying promising metal hydrides, (ii) predicting their stability and crystal structure and (iii) estimating the thermodynamics of hydrogen release. We use both solid-state and solution techniques to make promising metal hydrides predicted by theory.

This past year, a truly unique analytical capability has been added to the SNL research and development effort, called STMBMS. The essential features of STMBMS are illustrated in Figure 1, where a sample is placed within the reaction cell, the reaction cell is heated in a controlled manner and the identities and number densities of all gaseous species within the reaction cell are determined as a function of time. This basic information allows the rates of formation of all species to be determined as a function of time.

As part of our Center lead activities, we continued to provide technical leadership (setting directions, evaluating results) for the MHCoe Theory Group (TG) that makes use of first-principles methods to conduct materials discovery, provide thermodynamic and kinetic data for use by engineering and modeling

FIGURE 1. Layout of Simultaneous Thermogravimetric Modulated Beam Mass Spectrometry Apparatus

efforts, and suggest new directions for experimentalists and interpretation of their results. The TG consists of researchers at five institutions, comprising effectively four groups: SNL; Carnegie Mellon University and the University of Pittsburgh; University of Illinois at Urbana-Champaign; and the National Institute of Standards and Technology (NIST).

Results

Borohydrides and Related Materials

During Fiscal Year 2009 we completed extensive experimental and theoretical studies on borohydrides and related materials, particularly calcium borohydride $Ca(BH_4)_2$. The PEGS method was used to predict the enthalpies for the following two decomposition pathways for $Ca(BH_4)_2$:

Although the two reactions were predicted to have almost identical enthalpies, ~ 40 kJ/mol H_2 [1], the amounts of hydrogen released differ significantly in I and II and correspond respectively to 9.63% and 6.26% mass

fraction of hydrogen. A first-principles PEGS study and predictions of the structures of polymorphs of $\text{Ca}(\text{BH}_4)_2$ resulted in the correct identification of the beta-phase, observed in synthesis and cycling experiments. A PEGS and database search correctly found the ground state and several high-energy polymorphs which correspond to the high-temperature phases of $\text{Ca}(\text{BH}_4)_2$.

We conducted an experiment to estimate the enthalpy of desorption of $\text{Ca}(\text{BH}_4)_2$. Desorption isotherm measurements were carried out at two temperatures, 380°C and 354°C and desorption enthalpy was calculated using the van't Hoff formalism. The difficulty in achieving true equilibrium in this system may introduce uncertainty in the derived desorption enthalpy. Nonetheless, we estimate that desorption enthalpy to be in the range 60-100 kJ/mole H_2 , significantly larger than the desired 20-40 kJ/mole H_2 .

Our cycling measurements on pure and catalyzed $\text{Ca}(\text{BH}_4)_2$ revealed that the material suffers from a severe capacity loss on each subsequent cycle, as illustrated in Figure 2. We tested 30 different additives in order to decrease the desorption temperature and improve reversibility, but none were effective.

We speculated that formation of $\text{CaB}_{12}\text{H}_{12}$ might be the cause of the lack of reversibility for $\text{Ca}(\text{BH}_4)_2$. Using Sandia's high-pressure station, we showed that under the conditions known to promote partial reversibility in $\text{Ca}(\text{BH}_4)_2$, the mixture of CaH_2 and $\text{CaB}_{12}\text{H}_{12}$ cannot react to form $\text{Ca}(\text{BH}_4)_2$. This experiment shows that $\text{CaB}_{12}\text{H}_{12}$, if formed, would hinder reversibility.

Experiments in the MHCoe suggest that hydrogen desorption from borohydrides can lead to undesirable $\text{B}_{12}\text{H}_{12}$ intermediates that can act as hydrogen sinks. Using PEGS, we predicted the crystal structures for a number of alkali- and alkali-earth $\text{B}_{12}\text{H}_{12}$ compounds. The crystal structures are critical for the evaluation of the thermodynamic characteristics of the reactions involving these species [1]. To better understand the

FIGURE 2. Cycling Behavior of $\text{Ca}(\text{BH}_4)_2$ in the Presence of PdCl_2

experimental reactivity of $\text{B}_{12}\text{H}_{12}$ species, we synthesized a number of alkali and alkaline earth $\text{B}_{12}\text{H}_{12}$ salts. In collaboration with NIST, we validated the previously predicted structures. The crystal structures of monoclinic $\text{Na}_2\text{B}_{12}\text{H}_{12}$ is $P2_1/n$ and that for $\text{CaB}_{12}\text{H}_{12}$ is $C2/c$. We also demonstrated experimentally that the *closo*-dodecaborate salts are highly stable and cannot be dehydrogenated or hydrogenated under practical conditions.

Using STMBMS, we characterized the evolution of H_2 and other minor species as $\text{Ca}(\text{BH}_4)_2$ was heated from 20 to 1,000°C. Data from one series of these experiments is shown in Figure 3, which displays the rates of H_2 and BH_3 evolution as samples of uncatalyzed and $\text{PdCl}_2/\text{TiCl}_3$ catalyzed $\text{Ca}(\text{BH}_4)_2$ are heated through a series of isothermal steps between 120 and 500°C. It is clear that hydrogen is evolved in two distinct steps as the sample is ramped in temperature from 100-305°C. It is also clear that BH_3 is released along with H_2 in the desorption process. A detailed investigation of these effects is in progress.

During FY 2009, we made a decision to “down-select” $\text{Ca}(\text{BH}_4)_2$ as a potential bulk hydrogen storage material, removing it from further study. This decision was made after considering its poor reversibility, very high desorption temperature, and poor thermodynamics. Our attention then shifted to other borohydride materials, with a focus on $\text{Mg}(\text{BH}_4)_2$.

Magnesium borohydride is known to release ~14 weight percent hydrogen when decomposed to MgB_2 :

FIGURE 3. STMBMS Analysis of Desorption from Catalyzed $\text{Ca}(\text{BH}_4)_2$

In collaboration with University of Hawaii we demonstrated that reverse reaction of **III** occurs in good yield when MgB_2 is heated at 440°C and 70 MPa hydrogen pressure [4]. The importance of this result is that it sets a record for the highest hydrogen weight percent (~14 wt%) for a fully reversing metal hydride material. Work will be ongoing to reduce the pressure and temperature demands for this material.

In the past year we also examined the effects of carbon dopants on $\text{Mg}(\text{BH}_4)_2$. First, dopant levels of carbon were incorporated into the MgB_2 precursor by heating mixed powders of magnesium, boron and carbon. Thereafter, the as-made $\text{MgB}_{2-x}\text{C}_x$ pellets were reacted at 1,034 bar (15,000 psi) H_2 pressure while heating to synthesize C-doped $\text{Mg}(\text{BH}_4)_2$. Future work will focus on improving the yield of the doped borohydride fabricated in this way as well as incorporating transition metal dopants as potential ways to improve the thermodynamic and kinetic properties of $\text{Mg}(\text{BH}_4)_2$ for hydrogen storage.

A first-principles study of the thermodynamics of reactions in the Li-Mg-Ca-B-H system indicated several new reaction pathways involving $[\text{B}_{12}\text{H}_{12}]$ closo-borate. Structures of the closo-borate salts were predicted using the PEGS method and several were verified experimentally via diffraction and Rietveld refinement. The formation of these salts is shown to significantly impact the storage properties of $\text{Mg}(\text{BH}_4)_2$ and $\text{Ca}(\text{BH}_4)_2$, while several new ‘destabilized’ reactions involving the salts were identified. $\text{LiSc}(\text{BH}_4)_4$ formation and decomposition pathway were also investigated in collaboration with Caltech/Jet Propulsion Laboratory and SNL. Thermodynamic pathways were calculated using prototype structures generated using the PEGS method and are in agreement with experimentally observed decomposition products.

In collaboration with UTRC, we initiated a collaborative effort on mixed main-group – transition metal borohydride materials. The calculations predicted several stable compounds in the Li-Ti-BH₄ and Na-Ti-BH₄ systems. The synthesis of these compounds is challenging, however we made significant progress in isolating the unstable $\text{Ti}(\text{BH}_4)_3$, which serves as a starting material in these reactions. We also tested the effect of several Ti(III) precursors on the hydrogen desorption from LiBH_4 , $\text{Mg}(\text{BH}_4)_2$ and $\text{Ca}(\text{BH}_4)_2$ and showed that up to 3 wt% H_2 can be released at temperatures as low as 175°C.

Another approach we used to decrease the desorption temperatures of main group metal borohydrides is through complexation with ammonia. We explored $\text{Ca}(\text{BH}_4)_2\cdot\text{NH}_3$ and several mixed-heterometallic $\text{M}'\text{M}''(\text{BH}_4)_x\cdot\text{NH}_z$ systems (where M' and M''= Li, Na, Ca and/or Mg). Soloveichik *et al.* [5] have

recently demonstrated that the magnesium borohydride ammonia complex, $\text{Mg}(\text{BH}_4)_2(\text{NH}_3)_2$, exhibits improved hydrogen desorption properties compared to pure $\text{Mg}(\text{BH}_4)_2$, decreasing the dehydrogenation temperature by about 100°C. In our work, $\text{Ca}(\text{BH}_4)_2\cdot\text{NH}_3$, $\text{LiCa}(\text{BH}_4)_3\cdot\text{NH}_3$, and $\text{MgCa}(\text{BH}_4)_4\cdot\text{NH}_3$ were synthesized and displayed increased stability compared to the initial borohydrides. However, we found that significant amounts of ammonia was released upon heating. This finding indicates that the metal-ammonia bond in these complexes is more labile compared to $\text{Mg}(\text{BH}_4)_2(\text{NH}_3)_2$. In the case of $\text{Ca}(\text{BH}_4)_2\cdot\text{NH}_3$ the ammonia release is quantitative and pure $\beta\text{-Ca}(\text{BH}_4)_2$ was recovered after heating the adduct in vacuum at 195°C for 2 hours.

Interest in P compounds as hydrogen storage species has not been developed despite literature reports of compounds containing >9 wt% hydrogen. For example, $\text{Na}[\text{PH}_2(\text{BH}_3)_2]$ was reported to release hydrogen upon heating but the amount of hydrogen and the products of this thermal reaction were not explored [6]. We have developed novel methods for synthesizing phosphino-borane adducts and begun investigating the thermal decomposition chemistry.

A new family of inorganic hydrogen storage materials has been identified based of phosphino-borane salts. Depending on the nature of the alkali and alkaline earth metal salts, the hydrogen wt% can vary from 8.08 to 11.99. The sodium compound $\text{Na}[\text{PH}_2(\text{BH}_3)_2]$ (**1**) was initially synthesized at low temperature following eq **IV** [7].

Conversely, **1** was synthesized by the action of excess NaBH_4 on PH_4I . However, neither $\text{H}_3\text{P}\cdot\text{BH}_3$ or PH_4I are readily available starting materials and require the use of the extremely hazardous gas PH_3 . Therefore, an alternative route was devised using commercially available PCl_3 . The theoretical stoichiometry for the balanced reaction between phosphorus trichloride and sodium borohydride is given in eq **V**. Generation of boron trichloride and other side products are only speculative.

After varying solvent, reaction temperature, and the order of addition, the sodium phosphinoborane salt **1** was isolated and identified by ¹H and ³¹P NMR spectroscopy.

Efforts to fully characterize **1** are ongoing. Hydrogen release measurements on **1** have been performed using thermal gravimetric analysis and our coupled thermogravimetric analysis-mass spectrometer instrument. Preliminary results show that hydrogen release occurs near 150°C with some other additional species evolved in the process. The approximate mass

loss for **1** is near 6%. More efforts to identify the nature of the products and volatile species are underway.

Nanostructured Materials

We completed our collaboration with UTRC exploring methods to incorporate metal hydrides into nanostructured frameworks, with a focus on $\text{Ca}(\text{BH}_4)_2$ and C-aerogel. Precursor $\text{Ca}(\text{BH}_4)_2(\text{THF})_2$ was modified with alternative Lewis basic solvents such as pyridine, NH_3 , dimethoxyethane, and Et_2O . The products were characterized by beryllium dome X-ray diffraction and infra-red spectroscopy. If crystals were obtained, single crystal X-ray diffraction structural studies were undertaken to assist in identification. We attempted to “dip-coat” load the tetrahydrofuran (THF) adduct into yttria-stabilized zirconia (YSZ) and C-aerogel. However, it was unclear if any loading took place. We therefore turned to “incipient wetness loading” of $\text{Ca}(\text{BH}_4)_2(\text{THF})_2$ in a THF solution onto both YSZ and carbon aerogel (CA). This approach was more successful, loadings of up to 14% were observed.

Although incipient wetness yielded higher loadings, the calculated pore volume of the substrate indicated that the ceramic should be able to absorb more adduct. We exposed a CA sample to a concentrated solution of $\text{Ca}(\text{BH}_4)_2(\text{THF})_2$ in THF. After the aerogel was soaked in the solution, it was dried under vacuum at 100°C for 2 hours to remove the solvent. The results from this coated aerogel suggest that the amount of $\text{Ca}(\text{BH}_4)_2$ incorporated was over 50%. The desorption capacity was found to be low and significant improvement is necessary.

Gas-Phase Equilibria Modeling

We initiated the first theoretical studies of the effects of gaseous species (other than H_2) on the equilibrium of hydrogen desorption reactions. The composition of the gas-phase above a metal hydride was computed using a Gibbs free energy minimization method incorporated into a commercial thermodynamic modeling package known as FactSage. In this method, thermodynamic data taken from published thermodynamic data bases, such as the *JANAF Thermochemical Tables*, is combined with data for condensed-phase products available from similar public sources. Data for metal hydrides and some of their decomposition products, however, are often not available. To fill this gap we partnered with the research groups of Prof. David Sholl (Georgia Tech) and Prof. Karl Johnson (University of Pittsburgh), who developed computational methods based on density functional theory (DFT) to predict the thermochemistry of these materials.

Phase-equilibrium calculations were performed for several relatively well-understood hydride systems to assess the potential for the approach. These systems

include: LiNH_2 , $\text{LiNH}_2 + \text{LiH}$, and $\text{LiBH}_4 + \text{MgH}_2$. In addition, several destabilized reactions identified by Profs. Sholl and Johnson were examined, including $\text{LiBH}_4 + \text{C}$ and $\text{MgBH}_4 + \text{C}$, to determine whether these decompose to produce pure H_2 or significant concentrations of impurities are produced.

Some illustrative results are presented in Figure 4 for $\text{LiNH}_2 + \text{LiH}$ (left) and $\text{LiBH}_4 + \text{C}$ (right). The nominal reactions in the absence of LiH are: $2\text{LiNH}_2 \leftrightarrow \text{Li}_2\text{NH} + \text{NH}_3$ as well as $2\text{LiNH}_2 \leftrightarrow \text{Li}_2\text{NH} + 0.5\text{N}_2 + 1.5\text{H}_2$. However, when LiH is added, a new channel is possible: $\text{LiNH}_2 + \text{LiH} \leftrightarrow \text{Li}_2\text{NH} + \text{H}_2$. The results show that the NH_3 concentration is ~ 30 ppm for LiNH_2 alone, but that addition of LiH reduces NH_3 by nearly two orders of magnitude (~ 0.5 ppm) at temperatures desired for on-board regeneration with a fuel cell power train (~ 375 K).

FIGURE 4. Gas-Phase Composition at Equilibrium as a Function of Temperature for top: $\text{LiNH}_2 (+ \text{LiH})$; and bottom: $\text{LiBH}_4 + \text{C}$

In contrast, LiBH_4 destabilized by adding carbon does not produce fuel cell poisons like NH_3 . However, the formation of gas-phase hydrocarbons is possible. The nominal reaction is: $\text{LiBH}_4 + \text{C} \leftrightarrow \text{LiBC} + 2\text{H}_2$. However other possible reactions include:

The latter two reactions are thermodynamically favorable and redirect the hydrogen to form methane. Hydrogen does not become the thermodynamically favored gas-phase product until temperatures exceed 800 K.

Thermochemistry of Alane Complexes

We also performed calculations of the stability of AlH_3 with amines and ethers to help guide AlH_3 regeneration efforts of our partner Brookhaven National Laboratory. High-level computations using quantum-chemistry methods were used to obtain electronic energies, geometries, and vibrational frequencies for alane complexes. In particular, we employed the Bond Additivity Correction (BAC) suite of methods, developed by Sandia for the purpose of computing accurate heats of formation for small molecules. Other approaches, including the Gaussian-3 Method, DFT/B3LYP, and coupled-cluster methods, were also employed to calibrate the BAC methods and test for systematic errors.

Preliminary heats of formation and complexation energies reported last year were finalized this year by applying high-level methods described above to identify and compensate for systematic errors present in the lower-level (e.g. BAC-second-order Moller-Plesset perturbation theory [BAC-MP2]) methods. Heats of formation and complexation energies were determined for several 1:1 and 1:2 complexes of alane with electron donors, $\text{AlH}_3:\text{L}$ and $\text{AlH}_3:\text{L}_2$, where L represents an electron-donating ligand with a nitrogen or oxygen atom bound to Al. The nitrogen-containing ligands investigated include ammonia and several primary, secondary, and tertiary amines, while the oxygen-containing ligands comprise water, several alcohols, and a number of ethers. To determine thermochemical data for all complexes of interest, we applied the composite electronic structure method BAC-MP2.

Results for the heats of formation are shown in Figure 5. For the 1:1 complexes, Al:N bond strengths are found to range from 26–35 kcal/mol, while the Al:O bonds are significantly weaker, with bond strengths between 17 and 26 kcal/mol. In the 1:2 complexes, the Al:N and Al:O bonds are considerably weaker than in the 1:1 complexes, and total complexation energies for the 1:2 complexes are only about 40-50% higher than for their 1:1 counterparts. In the amine complexes, the complexation enthalpy tends to increase with the substitution level on the amine (primary < secondary

FIGURE 5. Trends in Heats of Formation (0 K) of Alane-Amine and Alane-Ether Complexes Predicted by DFT, BAC-G2, and the G3 Methods

< tertiary), with a similar trend observed for ether complexes, although steric effects destabilize some of the tertiary amine complexes. Based on these results, we conclude that the complex with triethylamine is the least stable of the amines and thus most easily decomposed to release AlH_3 , while of the ethers $\text{AlH}_3\text{O}(\text{C}_2\text{H}_5)_2$ has the smallest complexation energy.

Conclusions

Our work in FY 2009 can be summarized as follows:

- Completed a comprehensive PEGS study of the polymorphs of $\text{Ca}(\text{BH}_4)_2$, validated with experimental findings.
- Measured the enthalpy of desorption of $\text{Ca}(\text{BH}_4)_2$, found it to be 60-100 kJ/mole H_2 . This enthalpy is too large for $\text{Ca}(\text{BH}_4)_2$ to be considered a viable hydrogen storage material.
- Experimentally synthesized a variety of metal- $\text{B}_{12}\text{H}_{12}$ salts, thereby gaining understanding of their chemistry and role as intermediates in borohydride hydrogen storage.
- Found that $\text{CaB}_{12}\text{H}_{12}$ cannot be readily hydrogenated, explaining in part the poor cycling characteristics of $\text{Ca}(\text{BH}_4)_2$.
- Using STMBMS, found that $\text{Ca}(\text{BH}_4)_2$ releases substantial BH_3 along with H_2 when heated.
- “Down-selected” $\text{Ca}(\text{BH}_4)_2$, removing it from further study as a viable hydrogen storage material.

- Completed theoretical studies of the reaction pathways and thermodynamics of hydrogen desorption from $\text{Mg}(\text{BH}_4)_2$ and $\text{Ca}(\text{BH}_4)_2$.
- Developed a method to dope MgB_2 with carbon, thereby opening up a study of the effects of C on $\text{Mg}(\text{BH}_4)_2$ hydrogen release.
- Initiated a study of the properties of $\text{Ti}(\text{BH}_4)_3$, opening up future studies of mixtures of borohydrides with $\text{Ti}(\text{BH}_4)_3$.
- Synthesized ammonia additives of mixed metal borohydrides, found them to behave very differently from the ammonia adduct of magnesium borohydride.
- Initiated studies of mixtures of borohydrides and amides, found reduced thermal requirements for some compounds.
- Initiated studies of P-based hydrogen storage materials, found that $\text{Na}[\text{PH}_2(\text{BH}_3)_2]$ could be synthesized, and the compound releases hydrogen at $\sim 150^\circ\text{C}$.
- Developed a route to incorporating $\text{Ca}(\text{BH}_4)_2$ into C-aerogel with 50% loading, completing our work on the nanoframeworks project with UTRC.
- Completed phase equilibrium theoretical studies of the LiNH_2 , $\text{LiNH}_2 + \text{LiH}$ and $\text{LiBH}_4 + \text{C}$ systems. Found that gas phase species other than H_2 are important for determining reaction pathways and thermodynamics.
- Quantum chemical calculations show that the AlH_3 complex with triethylamine is the least stable of the amines and thus most easily decomposed to release pure AlH_3 , while of the ethers $\text{AlH}_3\text{O}(\text{C}_2\text{H}_5)_2$ has the smallest complexation energy.

The main focus of our future work will be improvement of existing materials and synthesis of new hydride materials with improved hydrogen storage characteristics. Future directions also will include extensive theoretical and experimental efforts towards gaining mechanistic understanding regarding the fundamental processes occurring during the cycling of metal hydrides.

Special Recognitions & Awards/Patents Issued

- Rönnebro, E.; Severa, G.; Jensen, C. Patent application. 2009.
- Jay Keller, the MHCoe Deputy Director and Sandia Hydrogen Program Manager, received the 2009 “DOE Hydrogen Program Special Recognition Award” for years of outstanding contributions to the DOE Hydrogen Program.

FY 2009 Publications/Presentations:

- “Role of Cation Size on the Structural Behavior of the Alkali-Metal Dodecahydro-*closo*-Dodecaborates”, J.-H. Her,

W. Zhou, V. Stavila, C.M. Brown and T.J. Udovic, *J. Physical Chemistry C*, **2009**, (in press) DOI: 10.1021/jp904980m.

- “Probing the structure, stability and hydrogen storage properties of calcium dodecahydro-*closo*-dodecaborate”, V. Stavila, J.-H. Her, W. Zhou, S. Hwang, Ch. Kim, L.A.M. Ottley, T.J. Udovic, submitted.
- “Alkali and alkaline-earth dodecahydro-*closo*-dodecaborates and their relevance to hydrogen storage” V. Stavila, J.-H. Her, M. Kartin, W. Zhou, S. Hwang, Ch. Kim, T.J. Udovic, 238th American Chemical Society meeting, Washington, D.C., August 16–20, **2009**.
- “Crystal structure of $\text{Na}_2\text{B}_{12}\text{H}_{12}$ and the role of cation size on the structural behavior of the alkali-metal dodecahydro-*closo*-dodecaborates”, J.-H. Her, W. Zhou, V. Stavila, C.M. Brown, T.J. Udovic, 238th American Chemical Society Meeting, Washington, D.C., August 16-20, **2009**.
- “Crystal structures of $\text{M}_n\text{B}_{12}\text{H}_{12}$ ($n=1,2$) compounds – possible intermediate species in the decomposition of $\text{M}(\text{BH}_4)_n$ ”, J.-H. Her, V. Stavila, M. Yousufuddin, W. Zhou, S.S. Jalisatgi, E. Rönnebro, T.J. Udovic, American Crystallographic Association Meeting, July 25–30, **2009**, Toronto, Canada.
- “ $\text{LiSc}(\text{BH}_4)_4$ as a Hydrogen Storage Material: Multinuclear High Resolution Solid State NMR and First-Principles Density Functional Theory Studies”, S. Hwang, C. Kim, R. Bowman, J. Reiter, J. Zan, J. Kulleck, H. Kabbour, V. Ozolins, E.H. Majzoub, *Journal of Physical Chemistry C* **113**, 9956-9968 (2009).
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- First-Principles Prediction of Thermodynamically Reversible Hydrogen Storage Reactions in the Li-Mg-Ca-B-H system, V. Ozolins, E.H. Majzoub, and C. Wolverton, *Journal of the American Chemical Society* **131**, 230-237 (2009).
- “Metastability and crystal structure of the bialkali complex metal borohydride $\text{NaK}(\text{BH}_4)_2$, L. Seballos, J.Z. Zhang, E. Rönnebro, J.L. Herberg, E.H. Majzoub, *Journal of Alloys and Compounds* **476**, 446-450 (2008).
- “A computational tool for complex ionic hydrides: global optimization using prototype electrostatic ground states”, E.H. Majzoub, Purdue Hydrogen Symposium 2009, Purdue University, Lafayette, Indiana, 22 April, 2009.
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IV.A.1d Chemical Vapor Synthesis and Discovery of H₂ Storage Materials: Li-Al-Mg-N-H System

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Project Start Date: March 1, 2005

Project End Date: February 26, 2010

Objectives

- To discover and develop advanced high capacity reversible hydrogen storage materials.
- To develop chemical vapor synthesis process for making nano particles for hydrogen storage.
- To develop reactive mechano-chemical process for synthesis and preparation of solid hydride materials.

Technical Barriers

This project addresses the following technical barriers from the Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) System Weight and Volume
- (E) Charging/Discharging Rates
- (J) Thermal Management

Technical Targets

As a partner in Metal Hydride Center of Excellence (MHCoE), the team at the University of Utah is responsible for exploring the potential of materials and reactions related to amide materials. Based on this charter of the team, the following technical targets are set:

- The reversible hydrogen storage capacity should be higher than 5 wt%,

- The temperature of dehydrogenation should be below 300°C, preferably between 80 to 150°C, and
- The kinetic rate of dehydrogenation and hydrogenation must be sufficiently rapid to meet the requirements of fuel cells.

Accomplishments

- Systemically investigated the effects of ball milling variables on reaction pathways of the LiNH₂-MgH₂ system. An optimized milling method for synthesizing pure LiMgN was developed.
- Conducted pressure-concentration-temperature (PCT) studies on hydrogenation properties of LiMgN and demonstrated that the hydrogenation of LiMgN is pressure sensitive.
- Systemically investigated the effect TiH₂ content on the dehydrogenation properties of the Mg-Ti-H system.
- Investigated the kinetics and thermodynamics of hydrogen storage reactions of nanostructured MgH₂-0.1TiH₂ by using PCT.
- Conducted exploratory studies on a new Li-B-Al-H system, which consists of Li₃AlH₆/LiBH₄ or Al/LiBH₄, as a potential reversible hydrogen storage material.
- Made Ti-doped nanosized Al powder using the chemical vapor synthesis (CVS) method, and tested the hydrogenation properties of NaH-Al (NaAlH₄) system using the CVS-prepared nanosized Al powder.

Introduction

As an integral part of the overall MHCoE project, the team at the University of Utah focuses on: the discovery, synthesis, and processing of nanocrystalline metal hydride materials for hydrogen storage applications.

The discovery of new metal hydrides is particularly crucial because the properties of materials or material systems available to date do not meet the targets set by DOE. The synthesis of nanocrystalline metal hydride materials has two aims: 1) improving the kinetic properties of both dehydrogenation and hydrogenation reactions through use of nano-scaled metal hydride materials; and 2) addressing the issues of mass production of selected metal hydrides that

will be needed in the future. The study of processing of metal hydrides is also necessary because the results have shown that the properties of metal hydrides during cycling have strong dependences on how these materials are processed or prepared.

Built on the accomplishments of Fiscal Year 2008, we focused on two material systems: ternary lithium magnesium nitride (LiMgN) and nano-structured Mg-Ti-H systems.

1. The effect of mechanical milling technique on the synthesis of pure LiMgN from the mixture of $\text{LiNH}_2\text{-MgH}_2$ was studied. An optimized condition for synthesizing pure LiMgN is proposed based on the results obtained. The hydrogenation properties of as-prepared LiMgN were further explored using PCT, X-ray diffraction (XRD) and nuclear magnetic resonance (NMR). The results demonstrated that the hydrogenation of LiMgN is pressure sensitive and a full charge of the samples (8 wt%) can be achieved only when the applied hydrogen pressure is higher than 140 bar at 180°C .
2. The effect of milling parameters and TiH_2 content on the dehydrogenation properties of Mg-Ti-H system was investigated. The results showed that dehydrogenation characteristics were significantly improved, releasing a large amount of hydrogen (~6.0 wt%) starting at 101°C , when 9.1 mol% TiH_2 was added and the samples were milled for 4 hours using a ultrahigh energy planetary mill under H_2 pressure. The isothermal desorption and absorption measurements on this sample demonstrated that the dehydrogenation and hydrogenation kinetics were rapid at 290°C measured by a PCT apparatus. This sample also showed an excellent cyclic stability upon hydrogenation/dehydrogenation tests.

In addition, a new Li-B-Al-H system, which consists of $\text{Li}_3\text{AlH}_6/\text{LiBH}_4$ or Al/LiBH_4 , is explored as a potential reversible hydrogen storage material. The results demonstrated that the presence of Al had a positive effect on the rehydrogenation of LiBH_4 at a much lower temperature than without aluminum addition.

Approach

The basic approach that we took for discovery of new materials is to select candidate materials for experiments based on fundamentals of inorganic chemistry as well as the predictions of theoretical thermodynamic modeling. We focused on possible reactions involving alanates, amides, nitrides and borohydrides. Once a candidate material is identified and prioritized, experimental screening of selected reactions will then be carried out.

A CVS process has been developed for the synthesis of nanosized metal hydride precursor powders. The

primary advantage of the CVS process is that it yields materials with homogeneity at the atomic level. The CVS process is also very flexible for fine tuning the chemical formula of materials.

A high-energy high-pressure reactive milling process has been developed for the synthesis of non-equilibrium metal hydride materials that cannot be synthesized otherwise. The Utah team is also assisting other partners in the MHCoe including Sandia National Laboratories, HRL Laboratories, and Brookhaven National Laboratory on the preparation of powder materials for detailed studies.

Results

1. Investigation of the Li-Mg-N-H (LiMgN) System

In FY 2008, experimental studies were carried out to characterize and explore the potentials of LiMgN . We were able to demonstrate that TiCl_3 -doped LiMgN can reversibly store up to 8 wt% H_2 by hydrogenating it in a custom-made autoclave. In FY 2009, we continued research on finding an optimized condition for synthesizing pure LiMgN from the mixture of LiNH_2 and MgH_2 , and PCT characterization of the hydrogenation properties of LiMgN .

a. Effects of Mechanical Ball Milling on Synthesis of Pure LiMgN from $\text{LiNH}_2\text{-MgH}_2$

To optimize the condition for preparing pure LiMgN , the effect of the mechanical milling technique on the dehydrogenation reactions of the mixture of $\text{LiNH}_2/\text{MgH}_2/4\text{wt}\%\text{TiCl}_3$ was investigated. Two different types of ball milling methods, namely low-energy ball milling (Jar-rolling) and high-energy ball milling (Spex Mill), were used in this study. The results are presented in the following.

The milled samples were characterized using thermal gravimetric analysis (TGA), XRD and Fourier transform infrared (FTIR). The results showed that there is no phase change during the whole low-energy ball milling process, and a relatively pure LiMgN is obtained after the sample was milled for 96 hours and then dehydrogenated. However, the high-energy ball milling technique initiates some reactions including the metathesis reaction between LiNH_2 and MgH_2 and release of H_2 and/or NH_3 during the milling process, which makes the subsequent dehydrogenation reactions more complicated and unexpected. Figure 1 shows the XRD patterns of a series of samples after Spex milling. It can be seen that the samples milled after first 0.5 hour (SP-0.25 and SP-0.5) only consist of the original LiNH_2 and MgH_2 phase, which indicates that following reaction does not take place at the earlier stage of high-energy ball milling, although the components on the right side

FIGURE 1. XRD patterns of a series samples for the mixture of LiNH_2 - MgH_2 -4wt% TiCl_3 after Spex mill treatments, where SP represents the Spex milling method and Hours represents the milling time.

of this reaction are predicted to be thermodynamically more stable than those on the left side.

After 1 hour Spex milling, although the MgH_2 phase is still dominating the XRD profile, the diffraction peaks of LiNH_2 become invisible. Two small peaks at 38° and 44° (2θ) are observed which can be assigned to the LiH phase based on the JCPDS database. This result indicates the presence of a new chemical reaction (reaction 1) between LiNH_2 and MgH_2 during the high-energy ball milling. However, the diffraction peaks of $\text{Mg}(\text{NH}_2)_2$, one of the expected products according to reaction 1, is undetectable by XRD, which can be attributed to the fact that the compound is easily deformed into an amorphous state under high-energy ball milling process. When the milling time is further prolonged to 2 or 4 hours, the diffraction peaks of MgH_2 also disappears completely, suggesting that MgH_2 is either consumed by the newly-formed $\text{Mg}(\text{NH}_2)_2$ or turned into an amorphous state due to the high-energy ball milling. At the same time, one broader peak at 41.5° is observed in the XRD profiles of samples SP-2 and SP-4, which can be assigned to MgNH phase according to the previous work.

The dehydrogenated SP-H samples are also rather complex due to the multi-steps reactions during the high-energy ball milling and subsequent dehydrogenation processes. The dehydrogenated products from the high-energy ball milled samples consist of multiphase structures, which were confirmed by the XRD and FTIR analysis. The results showed that pure LiMgN could not be made by using the high-energy ball milling technique. It is also worthwhile to

point out that the temperature and heating rate during the dehydrogenation process have critical effects on the components of the final products, which are under further investigation.

b. PCT Studies of the Hydrogenation Properties of LiMgN

Based on the above results, relatively pure LiMgN was prepared for further studies using PCT instrument and cyclic measurements. The isothermal adsorption experiments at 180°C for the as-prepared LiMgN under different hydrogen pressure were conducted in the Sieverts' type PCT instrument. The results showed that the hydrogenation of as-prepared LiMgN is pressure sensitive. To achieve a full charge of the sample, a hydrogen pressure higher than 140 bar is required. The hydrogenated sample contained $\text{Mg}(\text{NH}_2)_2$ rather than LiNH_2 confirmed by FTIR analysis, which is in agreement with our previous results.

A short cyclic measurement on the as-prepared LiMgN was also conducted using the PCT instrument. Figure 2 plotted the amount of hydrogen release/uptake versus cyclic number. It can be seen that a significant loss of the hydrogen capacity occurs during the cyclic experiments. It should be noted that the amount of the absorbed hydrogen is always higher than that of desorbed hydrogen at the same cycle which is a misleading result that will be further studied. More detailed dehydrogenation/rehydrogenation properties including reaction mechanisms will be also be studied further by the use of XRD, FTIR and solid-state NMR.

2. Investigation of the Nano-Scale Mg-Ti-H System

In FY 2008, we investigated the nano-scaled Mg-Ti-H mixtures prepared by high-energy-high-pressure milling. The analyses of TGA data indicated that the hydrogen

FIGURE 2. Cyclic Measurements of the As-Prepared LiMgN

release temperature for the $7\text{MgH}_2/\text{TiH}_2$ mixture was lower by about 255°C than that of as-received MgH_2 and fast dehydrogenation kinetics was achieved within 60 minutes. In FY 2009, we continued research on 1) effect of milling parameters on the dehydrogenation properties of Mg-Ti-H system, and 2) thermodynamics and kinetics of the hydrogen storage reactions of selected $\text{MgH}_2\text{-TiH}_2$ system (10:1) by a comprehensive PCT analysis.

a. Effect of Milling Parameters on the Dehydrogenation Properties of Mg-Ti-H System

The effects of milling parameters and TiH_2 content on the dehydrogenation properties of the Mg-Ti-H system were investigated by TGA and differential thermal analysis. The mixtures of MgH_2 and TiH_2 in various molar ratios were prepared using low energy and high energy ball-milling methods under an argon or hydrogen atmosphere. The results showed that dehydrogenation characteristics were significantly improved, releasing a large amount of hydrogen (~ 6.0 wt%) starting at 101°C , when 9.1 mol% TiH_2 was added and the samples were milled for 4 hours by ultrahigh energy planetary mill under 13.8 MPa hydrogen pressure. Figure 3 presented the activation energy (E_a) for the dehydrogenation of the milled Mg-Ti-H mixtures with various TiH_2 contents using the Ozawa-Flynn-Wall method. The most noticeable result is that the activation energy is reduced significantly when only 2 mol% of TiH_2 is added, and decreases gradually as the TiH_2 content is increased, which is similar to the plot of on-set temperature (at $5^\circ\text{C}/\text{min}$ heating rate) vs. TiH_2 content. In addition, the activation energy is further reduced from 81 to 68 kJ/mol when the molar ratio Mg:Ti was decreased from 50:1 to 4:1 (corresponding to 2 and 20 mol% of TiH_2 , respectively), although this lowers the hydrogen storage capacity to below 5 wt%. Thus, it can be concluded that the kinetics of dehydrogenation of Mg-Ti-H mixtures is improved as more TiH_2 is added.

FIGURE 3. Activation energy (E_a) for the dehydrogenation of milled Mg-Ti-H mixtures with various TiH_2 contents.

The $10\text{MgH}_2/\text{TiH}_2$ was selected for further investigation because it showed the lowest on-set temperature (at $5^\circ\text{C}/\text{min}$ heating rate) at around 101°C and a reasonable reaction rate with over 6 wt% theoretical H_2 capacity. The effects of milling technique (low-energy or high-energy milling) and milling time on the dehydrogenation behavior of the Mg-Ti-H systems are also investigated.

b. PCT Studies on the Hydrogen Storage Properties of the Nano-Scaled $\text{MgH}_2\text{-0.1TiH}_2$ System

To improve the kinetics and thermodynamic properties of MgH_2 during dehydrogenation-rehydrogenation cycles, a nano-structured $\text{MgH}_2\text{-0.1TiH}_2$ material system prepared by ultrahigh-energy-high-pressure (UHEHP) mechanical milling was investigated. The mixtures of MgH_2 and TiH_2 in molar ratio of 10:1 were milled using a UHEHP ball milling device under 13.8 MPa hydrogen pressure for 4 hours at room temperature. High-resolution transmission electron microscopy and scanning transmission electron microscopy analysis showed that the grain size of the milled $\text{MgH}_2\text{-0.1TiH}_2$ powder is approximately 5-10 nm with TiH_2 distributed uniformly among the MgH_2 particles.

The isothermal desorption and absorption measurements by a PCT apparatus demonstrated that the dehydrogenation and hydrogenation kinetics of the milled $\text{MgH}_2\text{-0.1TiH}_2$ powder are rapid at 290°C . More importantly, the milled $\text{MgH}_2\text{-0.1TiH}_2$ material shows an excellent cyclic stability upon hydrogenation/dehydrogenation tests. A total of 80 cycles were performed and the results are presented in Figure 4A, showing that there was little loss in hydrogen storage capacity after 80 cycles. The kinetic data of the first and last cycles from the cyclic measurements were extracted and plotted as shown in Figures 4B and 4C. It is obvious that the kinetic of both hydrogenation and dehydrogenation remained intact from the first to the last cycle. Thus, in this respect, $\text{MgH}_2\text{-0.1TiH}_2$ is superior to un-doped nano- or micro-scaled MgH_2 , which loses its hydrogen storage capacity during cycling. The above results demonstrate that both the nanosize and the addition of TiH_2 contribute to the improvement of the kinetics of dehydrogenation and hydrogenation of MgH_2 .

In addition to the kinetic aspect, the pressure-composition-isothermal results showed that the ΔH value of the dehydrogenation of the milled $\text{MgH}_2\text{-0.1TiH}_2$ is lower than that of MgH_2 . The ΔS value is, however, also lower than that of commercial pure MgH_2 . Therefore, the net effect of the use of nanosized particles and the addition of TiH_2 had minimum effect on P_{eq} – the equilibrium pressure of dehydrogenation in the temperature range tested.

FIGURE 4. A) Cyclic measurements of the milled $\text{MgH}_2/0.1\text{TiH}_2$; B) Isothermal dehydrogenation curves for the milled $\text{MgH}_2/0.1\text{TiH}_2$ under 1 kPa hydrogen pressure at 300°C during the 1st and 80th cyclic measurements, respectively; C) Isothermal hydrogenation curves for the dehydrogenated $\text{MgH}_2/0.1\text{TiH}_2$ under 2 MPa hydrogen pressure at 300°C during the 1st and 80th cyclic measurements, respectively.

3. Investigation of Li-B-Al-H System for Reversible Hydrogen Storage

In FY 2009, a new Li-B-Al-H system, which consists of $\text{Li}_3\text{AlH}_6/\text{LiBH}_4$ or Al/LiBH_4 , was explored as a potential reversible hydrogen storage material. LiBH_4 and $\text{Li}_3\text{AlH}_6/\text{Al}$ were mechanically milled to form Li-Al-B-H systems by low-energy milling. The dehydrogenation and rehydrogenation properties were investigated by the use of XRD, TGA and solid-state NMR. The analysis of TGA data showed that the TiCl_3 -doped $\text{Li}_3\text{AlH}_6/2\text{LiBH}_4$ and $0.5\text{Al}/\text{LiBH}_4$ can release ~ 8.8 and ~ 8.4 wt% H_2 up to 450 and 380°C , with ~ 3.8 and ~ 5.8 wt% of hydrogen recovery, respectively. The XRD and solid-state NMR results showed that the dehydrogenated products are composed of LiH and AlB_2 . It has been determined by the NMR that the addition of Al has resulted in a remarkable improvement of the reversible dehydrogenation of LiBH_4 , and its reactivity has been substantially changed when smaller amount of aluminum (0.5 vs. 0.05 mol% Al) was added under the same H_2 release/uptake conditions. Although some unknown species has been found in the dehydrogenation process and the hydrogenation was only partially occurred in the limited temperature and pressure ranges, we believed that the presence of Al could be an important factor to make the rehydrogenation happen for LiBH_4 at a much lower temperature, at which dehydrogenation product from LiBH_4 alone does not show any degree of rehydrogenation.

4. Chemical Vapor Synthesis of Ti-doped Al Nanopowders and its Hydrogenation Properties in NaH-Al-H_2 (NaAlH_4) System

One of the objectives of our project is to demonstrate the feasibility of making nanosized metal or metal hydride precursor materials using the CVS method. In FY 2008, Ti-doped nano aluminum powder was successfully synthesized using the premixed 4 mol% $\text{TiCl}_3\text{-AlCl}_3$ precursor. Energy dispersive X-ray spectroscopy and XRD results showed that Ti was distributed uniformly in the nano-sized aluminum powder and small amount of Al_3Ti intermetallic compound was formed in the product powder. In FY 2009, the hydrogenation properties of NaAlH_4 system using the CVS-prepared nano Al powders were tested. The results indeed showed that a better dehydrogenation/hydrogenation kinetics is achieved compared to that of using commercial Al or NaAlH_4 powders.

Conclusions and Future Directions

Summary and Conclusions

- The mechanical milling processing variables have critical effects on synthesis of LiMgN from the mixture of LiNH_2 and MgH_2 . The likely reaction pathways during the high-energy ball milling were identified based on the XRD and FTIR results.
- The PCT results showed that the hydrogenation of LiMgN is pressure sensitive. Hydrogen pressure higher than 140 bar is required to fully charge LiMgN ($\sim 8\text{wt}\%$).
- The isothermal desorption and absorption measurements of nanostructured $\text{MgH}_2\text{-}0.1\text{TiH}_2$ demonstrated that the dehydrogenation and hydrogenation rates are very rapid at 290°C . This material also showed an excellent cyclic stability upon hydrogenation/dehydrogenation tests.
- A new Li-B-Al-H system, which consists of $\text{Li}_3\text{AlH}_6/\text{LiBH}_4$ or Al/LiBH_4 , is explored and investigated as a potential reversible hydrogen storage material.
- The CVS method is used to produce Ti doped nano Al powders, and the hydrogenation properties of NaAlH_4 system using the CVS-prepared nano Al powders were tested.

Future Directions

- Fully understand the reaction mechanisms of LiMgN during cyclic hydrogenation and dehydrogenation reactions.
- Study the different catalysts on improving the kinetic properties of the hydrogen storage reactions using LiMgN .

- Further explore means to reduce the temperature of dehydrogenation of $\text{MgH}_2\text{-TiH}_2$ systems.
- Produce sufficient quantities of Ti-doped nano Al powders as precursors for regeneration of AlH_3 .

Special Recognitions & Awards/Patents Issued

1. Dr. Jun Lu, a Postdoc fellow of Professor Zak Fang, was selected for “Garr Cutler Energy Prize” at the University of Utah, 2008 for his research work on reversible hydrogen storage materials.

FY 2009 Publications/Presentations

1. Jun Lu, Young Joon Choi, Zhigang Zak Fang, Hong Yong Sohn and Ewa Ronnebro, “Hydrogen Storage Thermodynamic and Kinetic Properties of Nanosized $\text{MgH}_2\text{-0.1TiH}_2$ Prepared by Reactive Mechanical Milling”, To be submitted to *J. Am. Chem. Soc.*
2. Young Joon Choi, Jun Lu, Hong Yong Sohn, Zhigang Zak Fang and Ewa Ronnebro, “Effect of Milling Parameters on the Dehydrogenation Properties of the Mg-Ti-H system”, To be submitted to *J. Phys. Chem. C*.
3. Young Joon Choi, Jun Lu, Hong Yong Sohn, Zhigang Zak Fang, Chul Kim, Robert C. Bowman Jr., and Son-Jong Hwang, “Hydrogen Storage Properties of a Li-Al-B-H System”, *In preparation*.
4. Jun Lu, Young Joon Choi, Vineet Kumar, Zhigang Zak Fang, and Hong Yong Sohn, “Study of Phase Transformation of MgH_2 during High-pressure-high-energy Mechanical Milling”, *In preparation*.
5. Jun Lu, Young Joon Choi, Zhigang Zak Fang, and Hong Yong Sohn, “Effect of Mechanical Milling on the synthesis of Pure LiMgN and its Hydrogen Storage Properties”, *In preparation*.
6. Jun Lu, Zhigang Zak Fang, Young Joon Choi, Hong Yong Sohn, Robert C. Bowman Jr., Son-Jong Hwang and Chul Kim, “Study of the Reaction Mechanism of Li-Al-N-H System during the Hydrogenation Process”, *J. Power Sources*, 185, 1354-1358, 2008.
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10. Jun Lu, Zhigang Zak Fang, Young Joon Choi, H. Y. Sohn, and Eva Ronnebro, “Hydrogen Storage Properties of Mg-Ti-H System Prepared by Mechanical Milling”, presented during 2009 MRS Spring Meeting, San Francisco, CA, April 15, 2009.
11. Zhigang Z. Fang, Jun Lu, Brady Butler, and Hong Yong Sohn, “Hydrogen Storage Materials Based on Li-Al-Mg-N Systems”, International Symposium on Metal-Hydrogen Systems, MH2008, Reykavik, Iceland, June 24-28, 2008.
12. Zhigang Zak Fang et al “Hydrogen Storage Properties of Li-Mg-N-Al-H System”. AsiaNano 2008. Biopolis, Singapore. November 3-7, 2008. (Invited talk).

IV.A.1e Aluminum Hydride Regeneration

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Project Start Date: October 1, 2005

Project End Date: June 30, 2010

Objectives

Develop an onboard vehicle storage system meeting DOE's targets that uses aluminum hydride for storing hydrogen.

- Produce aluminum hydride (AlH_3) material with a hydrogen storage capacity greater than 9% gravimetric ($\text{kg-H}_2/\text{kg}$) and 0.13 $\text{kg-H}_2/\text{L}$ volumetric.
- Develop practical and economical processes for regenerating aluminum hydride.
- Provide assistance in designing onboard fuel tank storage system for better than 6% gravimetric, 0.07 $\text{kg-H}_2/\text{L}$ volumetric hydrogen storage capacities and well-to-wheels efficiencies greater than 60%.

Technical Barriers

This project addresses the following technical barriers from the Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) System Weight and Volume
- (D) Durability/Operability
- (E) Charging/Discharging Rates

Technical Targets

The 2010 and 2015 hydrogen storage targets are listed in Table 1 along with our 2009 status using AlH_3 . The well-to-wheels efficiency listed in Table 1 under the column for 2009 Status were taken from an independent analysis of an aluminum hydride storage system by R.K. Ahluwalia of Argonne National Laboratory. This

analysis was presented at the 2008 Hydrogen Annual Program Review and was based, in part, on data supplied by Brookhaven National Laboratory (BNL). Argonne's analysis assumes a 70 wt% aluminum hydride slurry, and uses trimethylamine as the stabilizing agent for regenerating aluminum hydride in determining the 55% well-to-wheels efficiency. The reactor temperature of 120°C listed in the row for full flow rate is the most recent value measured by Brookhaven that meets the DOE fuel flow target, and is for a 40 wt% aluminum hydride slurry (see Figure 4). The gravimetric storage parameter of 0.036 is a measured value from a 40 wt% slurry consisting of 9 wt% aluminum hydride particles.

TABLE 1. Progress in Meeting Technical Hydrogen Storage Targets
Aluminum Hydride Regeneration

Storage Parameter	Units	2010/2015 Target	2009 Status
Gravimetric	wt% H_2	0.06/0.09	0.036
Volumetric	$\text{kg H}_2/\text{L}$	0.045/0.081	0.05
Full Flow Rate (temperature)	(g/s)/kW °C	0.02 80	0.02 120
Well-to-Wheels Efficiency	kW- H_2 /kW	60%	55%
Refueling Time	min	3/2.5	TBD

TBD - to be determined

Accomplishments

Progress was realized in Fiscal Year 2009 towards meeting DOE's storage targets with the following four findings:

- (1) Several new pathways were identified to form AlH_3 adducts from H_2 and catalyzed aluminum (Al^*):
 - Quinuclidine alane:
 $\text{C}_7\text{H}_{13}\text{N} + \text{Al}^* + 3/2\text{H}_2 \rightarrow \text{C}_7\text{H}_{13}\text{N-AlH}_3$
 - Dimethylethylamine alane:
 $\text{C}_4\text{H}_{11}\text{N} + \text{Al}^* + 3/2\text{H}_2 \rightarrow \text{C}_4\text{H}_{11}\text{N-AlH}_3$
 - Hexamine alane:
 $\text{C}_6\text{H}_{12}\text{N}_4 + \text{Al}^* + 3/2\text{H}_2 \rightarrow \text{C}_6\text{H}_{12}\text{N}_4\text{-AlH}_3$
 - Trimethylamine alane:
 $\text{C}_3\text{H}_9\text{N} + \text{Al}^* + 3/2\text{H}_2 \rightarrow \text{C}_3\text{H}_9\text{N-AlH}_3$
- (2) Improved adduct separation by introducing triethylamine (TEA) transamination step for the recovery of AlH_3 from AlH_3 adducts.
- (3) Two low energy pathways identified for complete regeneration of AlH_3 using trimethylamine (TMA) and dimethylethylamine (DMEA) (each step verified independently).

- (4) Initial results on H₂ evolution rates from AlH₃ in slurries showed promising results for Ti catalyzed AlH₃ in C₁₀H₂₂O₂.

Introduction

A cornerstone of the hydrogen economy is the hydrogen fuel cell car. Although there are many barriers before consumers fully accept the fuel cell car, a key barrier is the poor volumetric energy densities of conventional hydrogen storage media. Solid-state storage in metal hydrides or complex hydrides offers enhanced volumetric hydrogen densities, however they have either poor gravimetric capacity (<4 wt%) or release hydrogen at temperatures (>300°C) that are impractical for a fuel cell car. A class of kinetically stabilized hydrides (e.g. AlH₃, LiAlH₄, Mg(AlH₄)₂) offers some new hope with high volumetric (>80g H₂/L) and gravimetric (>10 wt%) energy densities and with low decomposition temperatures (<120°C). However, these materials typically have very high hydrogenation pressures (>1 kbar) and are generally prepared from costly organometallic reactions. Therefore, Brookhaven has been interested in developing new low-cost methods to regenerate these kinetically stabilized hydrides from spent (hydrogen depleted) material and hydrogen gas. Of the high capacity, kinetically stabilized hydrides one of the most promising storage materials is AlH₃. Reports of molecular alane (e.g. AlH₃, Al₂H₆ and Al₄H₆) formation from aluminum and hydrogen under a variety of conditions support the recent suggestion that transient alane species form on the surface of catalyzed aluminum in the presence of hydrogen gas [1]. Based on this hypothesis, last year we developed a method to prepare alane and alane adducts by “stabilizing” the transient alane formed on the catalyzed aluminum surface [2]. In Fiscal Year 2009 various amine alanes were directly synthesized from aluminum and hydrogen gas in solution at low pressures and temperatures, and we began investigating aluminum hydride slurries.

Approach

The research direction under the Metal Hydride Center of Excellence (MHCoE) being pursued by Brookhaven is to form hydride materials on the aluminum particle surfaces, and then stabilize these surface hydrides with chemical agents such as amines, ethers and/or lithium hydride. This approach is very similar to the well-studied cycling of sodium alanate with aluminum, where sodium hydride functions as the stabilizing agent. The main difference being that this research focuses on forming the hydride on the aluminum surface in a liquid phase rather than a high pressure hydrogen gaseous environment. The

advantages are that surface alane formation lowers considerably the hydrogenation pressure, and the liquid phase offers better thermal management and mass transport. The research plan therefore calls for first identifying the appropriate adduct(s), solvents, catalysts, and temperature and pressure conditions for making and “stabilizing” the aluminum hydride adduct in an effective and energy efficient manner. The second step, necessary to complete the regeneration cycle, is hydride recovery from the newly formed hydride-adduct. In addition to the regeneration studies, we have recently started to investigate slurry aluminum hydride decomposition kinetics as a function of temperature, catalysts and slurry type. The use of slurries is one way to meet the three minute refueling target. However, to improve the well-to-wheel efficiencies to above 60%, the aluminum hydride decomposition temperature needs to be lowered to less than 100°C, and more energy efficient regeneration schemes are still required.

Results

Regeneration of AlH₃ – Stabilization. The Ti-catalyzed Al (henceforth denoted as Al*) was prepared by first synthesizing AlH₃ in an ethereal reaction between LiAlH₄ and AlCl₃. The TiCl₃ catalyst was added to the diethyl ether solution and filtered to remove the LiCl precipitate. The filtrate (AlH₃ + Ti + Et₂O) was dried and decomposed under vacuum at 373 K for one hour to remove the ether and decompose the hydride. The addition of Ti significantly destabilized the hydride (AlH₃) and decomposition occurred readily at room temperature using a nominal concentration of 2 mol% Ti. Powder X-ray diffraction of the dried and decomposed material showed no evidence of the hydride phase and confirmed that the final product was pure Al*.

Hydrogenation experiments were performed in a 300 ml Parr Instruments (P <100 bar) and a PPI (P >100 bar) stainless steel stirred reactor. The reactors were loaded and sealed in an Ar-filled glove box with typically between 1-1.5 g of Al*. Thermocouples were used to monitor the internal and external temperatures and the gas pressure in the reactor was measured using a pressure transducer.

Figure 1 shows the formation of AlH₃-TMA occurring at moderate pressures (~250 bar) in toluene after a 10-12 hour incubation period. The hydrogenation reaction is shown in equation (1):

This reaction occurs more quickly in ether solvents such as diethyl ether and tetrahydrofuran (THF) and exhibits a shorter incubation period. TMA is a gas under ambient conditions, while the TMA-AlH₃ product is a crystalline solid that appears to be soluble in toluene, diethyl ether and THF.

FIGURE 1. Formation of Trimethylamine Alane as a Function of Time at 298 K in THF

Figure 2 shows that the formation of AlH_3 -DMEA occurring readily at low pressures (<60 bar) after an 8-10 hour incubation period. The hydrogenation reaction is shown in equation (2):

In this case the amine precursor ($\text{C}_4\text{H}_{11}\text{N}$) and the amine alane product ($\text{AlH}_3\text{-C}_4\text{H}_{11}\text{N}$) are both liquids.

Figure 3 shows that the formation of AlH_3 -quinuclidine occurring at low pressures (<62 bar) with an incubation period of around 5 hours. The hydrogenation reaction is shown in equation (3):

Both AlH_3 -TMA and AlH_3 -quinuclidine are solids at room temperature. AlH_3 -quinuclidine and AlH_3 -TMA are at least partially soluble in the ether solvents, but the solid product can easily be distilled from the solution.

Regeneration of AlH_3 – Adduct Separation. The previous results demonstrate that a number of different ligands can be used to stabilize AlH_3 . A second step, where the alane adduct is separated and AlH_3 is recovered, is required to complete the regeneration cycle. Despite numerous attempts most of the alane amines that form readily by direct hydrogenation can only be separated at high temperatures where AlH_3 is unstable.

The challenge of recovering intact AlH_3 from the alane amine can be overcome by introducing a transamination step. In this process the more stable alane amine is displaced by a second alane amine that is less thermally stable. One example of a less stable alane amine is AlH_3 -TEA (TEA = triethylamine). AlH_3 -TEA is a liquid at room temperature and can be separated into

FIGURE 2. Formation of Dimethylethylamine Alane as a Function of Time at 296 K in THF

FIGURE 3. Formation of Quinuclidine Alane as a Function of Time at 298 K in THF

AlH_3 (solid) and TEA (liquid) by heating to 75°C under a nitrogen sweep. The full regeneration procedure for AlH_3 can be envisioned as shown below where NR_3 represents an amine:

Alane Slurries. A constant volume Sieverts apparatus with a controlled temperature (30 - 150°C) oil bath was used to determine the hydrogen release rates of alane slurries. The liquid carrier used for the slurry tests was diethylene glycol dibutyl ether (DEGDBE). DEGDBE was initially selected because it is water immiscible, has a very low vapor pressure, and mixes well with (wets) aluminum hydride particles. At the reactor temperature of 150°C the

vapor pressure of DEGDDBE was measured to be less than 1 mbar in the Sieverts. For reference, 0.3 g of dry aluminum hydride, consisting of 9 wt% hydrogen upon decomposition, raises the pressure in the Sieverts to just over 500 mbar(s). The experiment consisted of testing three samples; 1) dry 0.3 g AlH_3 , 2) 0.3 g of AlH_3 in 40 wt% slurry with no catalyst, and 3) 0.3 g of AlH_3 in 40 wt% slurry with 0.1% Ti catalyst addition. All samples tested raised the pressure in the Sieverts to 500 mbar which indicates complete decomposition. The major difference in this test was the time to reach complete decomposition. Figure 4 plots the hydrogen release at 120°C for the two slurries tested, and shows the significant increase in decomposition rates with the use of 0.1% Ti catalyst. Further tests will be directed towards slurries consisting of larger sized aluminum hydride particles to increase the allowable solid mass loading of the slurry. Furthermore, the inert DEGDDBE liquid carrier will be replaced by a liquid that also releases hydrogen. The target is to formulate an alane slurry with greater than 8 wt% hydrogen release at 100°C.

Conclusions and Future Directions

At this point we have concluded that many alanes of tertiary amines may be synthesized at relatively modest hydrogen pressures using activated Al, provided steric effects are not inhibiting. Thus simple amines such as DMA and DMEA react readily, as well as more complex, cyclic amines such as TEDA, quinuclidine and hexamine where the functional N atom is exposed and in a constrained spatial configuration. In conclusion, this year's research has reinforced the concept of using alane as a hydrogen storage material for fuel cell vehicles. However several technical barriers need to be overcome before an alane storage system becomes viable. These

barriers define the future direction of alane research at BNL, and are listed as follows.

- High yield, regeneration of AlH_3 with E penalty ≤ 73 kJ/ H_2 (30% of fuel energy).
- Continue investigation of alane slurries and liquid carriers for 8 wt% H_2 storage at temperatures around 100°C.
- Work with partners (Argonne National Laboratory) to determine mass balance and energy cost for alane recovery from spent aluminum.
- Work with partners (MHCoE) on safety and engineering of alane regeneration and slurry systems.

Special Recognitions & Awards/Patents Issued

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2. J. Graetz, "New Approaches to Hydrogen Storage" *Chem. Soc. Rev.*, **38** 73 (2009).
3. J. Graetz, J. Wegrzyn and J.J. Reilly, "Regeneration of lithium aluminum hydride (LiAlH_4)", *J. Amer. Chem. Soc.* **130** 17790 (2008).
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8. J. Graetz, "Regeneration of Metastable Hydrides", *LANL-AIST/NEDO Workshop on Hydrogen Storage and Fuel Cells*, San Diego, CA, 2008.
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FIGURE 4. H_2 Release at 120°C from 40 wt% AlH_3 Slurry With/Without Ti Catalyst

10. J. Graetz “Direct Alane Formation under Mild Conditions”, *American Ceramics Society - Materials Innovations in an Emerging Hydrogen Economy conference*, Cocoa Beach, Florida, 2008.

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IV.A.1f Electrochemical Reversible Formation of Alane

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Project End Date: October 1, 2011

Objectives

- Develop a low-cost rechargeable hydrogen storage material with cyclic stability and favorable thermodynamics and kinetics fulfilling the DOE onboard hydrogen transportation goals.
- Develop an economical method to regenerate aluminum hydride (alane - AlH_3) from aluminum metal, since aluminum hydride has a gravimetric capacity of 10 wt% and volumetric capacity of 149 g/L H_2 and desorption temperature: $\sim 60^\circ\text{C}$ to 175°C (depending on particle size and the addition of catalysts) meeting the 2010 DOE targets.

Technical Barriers

This project addresses the following technical barriers from the Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) System Weight and Volume
- (B) System Cost
- (C) Efficiency
- (R) Regeneration Processes

Technical Targets

- Develop a low-cost rechargeable hydrogen storage material fulfilling the DOE transportation goals.
- AlH_3 is a viable system that fulfills the DOE 2010 transportation goals.
- Avoid the impractical high pressure needed to form AlH_3 .

- Avoid chemical reaction route of AlH_3 that leads to the formation of alkali halide salts such as LiCl .
- Utilize electrolytic potential to translate chemical potential into electrochemical potential and drive chemical reactions to form AlH_3 .

Accomplishments

- Continued multiple electrochemical cells systematic study.
- Developed a methodology to confirm the generation of AlH_3 in the cell.
- Succeeded in producing large quantities of AlH_3 -triethylenediamine (TEDA) complex, electrochemically.
- Recovered alane from alane-tetrahydrofuran (THF) adduct.
- Developed ways to recover pure alane from solvent.
- Produced gram quantities of alane, electrochemically.
- Working on the efficiency aspects of the cycle.

Introduction

Discovering efficient and economic methods for storing hydrogen is critical to advancing the hydrogen economy. The DOE is supporting research to demonstrate viable materials for on-board hydrogen storage. Researchers worldwide have identified a large number of compounds with high hydrogen capacity that can fulfill these gravimetric and volumetric requirements. Unfortunately, the majority of these compounds fail to meet the thermodynamic and kinetic needs for on-board storage systems. Alane has the gravimetric (10.1 mass% H_2) and volumetric (149 kg H_2/m^3) density. In addition, rapid hydrogen release from alane can be achieved using only the waste heat from a fuel cell or a hydrogen internal combustion engine [1]. The main drawback to using alane in hydrogen storage applications is unfavorable hydriding thermodynamics. The direct hydrogenation of aluminum to alane requires over 10^5 bars of hydrogen pressure at room temperature as shown in equation (1). The impracticality of using high hydriding pressure has precluded alane from being considered as a reversible hydrogen storage material.

The typical formation route of alane is through the chemical reaction of lithium alanate with aluminum chloride in diethyl ether. This reaction yields dissolved

alane etherate, $\text{AlH}_3 \cdot \text{Et}_2\text{O}$, and precipitates lithium chloride. Alane can be separated from the ether by heating *en vacuo* [2-5]. The synthesis of AlH_3 by these methods result in the formation of alkali halide salts such as LiCl . The formation of these salts becomes a thermodynamic sink because of their stability. For a cyclic process, lithium metal must be recovered from lithium chloride by electrolysis of a LiCl/KCl melt at 600°C and costing at least -429 kJ/mol of energy equivalent to the heat of formation and heat of fusion of LiCl [6].

Approach

Our approach has pursued a more economically and thermodynamically cost-effective formation and regeneration route of alane than conventional chemical methods. Our process utilized electrolytic potential, E , to drive chemical reactions to form AlH_3 . The equilibrium potential (E) is determined from the Gibbs' free energy change (ΔG) using equation 2:

$$\Delta G = -nFE \quad (2)$$

Where n is number of electrons transferred and F is the Faraday constant of 96,485 coulombs.

However, AlH_3 is extremely reactive in water and air, forbidding the use of all protic solvents. For this reason, a novel route using a non-aqueous solvent system is needed. Polar aprotic solvents such as THF or diethyl ether with dissolved ionic compounds such as NaAlH_4 or LiAlH_4 were used to form a conductive electrolyte that can be used in the electrochemical cell to form alane. For example, NaAlH_4 is dissolved in this solvent, forming the ionic solution ($\text{Na}^+/\text{AlH}_4^-/\text{THF}$) which is used as an electrolyte. The cycle, shown in Figure 1, utilizes electrochemical potential to drive the formation of alane and alkali hydride (e.g. LiH , NaH and KH) from an ionic alanate salt. The starting alanate is regenerated by direct hydrogenation of spent aluminum with the byproduct alkali hydride (e.g. NaH) in the presence of titanium catalyst under moderate hydrogen pressure ($\sim 100 \text{ bars}$), a well studied reaction [7-10].

Though not directed at the regeneration of alane, elaborate research and extensive studies on the electrochemical properties of this type of electrolyte has been reported [11,12]. Although attempts in the past were made to synthesize alane electrochemically, none have shown isolated material or a characterized alane product [13-15]. Thermodynamic properties of the above electrolyte, along with cyclic voltammetry were the basis for conducting this electrochemical process. Thermodynamic calculations were made to determine the reduction potentials for possible electrochemical reactions of NaAlH_4 in an aprotic solution (THF) with an aluminum electrode. From the half reaction potentials, the cell voltage for alane formation was

Non-Aqueous Solution Regeneration Cycle

FIGURE 1. Reversible alane regeneration cycle. All components of the electrochemical process can be recycled to continually afford a viable solid state storage material for the hydrogen economy.

calculated and a theoretical cyclic voltammogram was constructed.

Results

At least two separate reaction mechanisms can produce alane at the aluminium electrode. One possible mechanism is the oxidation of the AlH_4^- ion to produce alane, an electron, and hydrogen as shown in equation (3):

Another possible mechanism is the reaction of AlH_4^- with the aluminium anode to form alane. In this reaction route, the evolution of hydrogen is suppressed and the reaction is expected to consume the Al electrode as in equation (4):

The different conditions of reactions 3 and 4 depend on their Gibbs free energy (ΔG). ΔG for reactions (3) is $-167.1 \text{ kJ/mol} \cdot \text{AlH}_3$ and for reactions (4) is $-113.7 \text{ kJ/mol} \cdot \text{AlH}_3$. Since Na^+ is the counter ion of AlH_4^- the respective equilibrium potentials are -1.73 for reaction (3) and -1.57 V for reaction (4) vs. standard hydrogen electrode. Experimental observations confirmed that under the conditions of reaction 4, the anode is consumed.

During these experiments, the current was steady and increased slightly with time. The electrochemical production of alane is found not to be slowed by the formation of AlH_3 . The surface area of the electrodes and the cell current are observed to be the rate limiting

factors. In contrast to previous reports, no visible signs of alane perception in solution were observed [15] and the alane produced by our method is completely dissolved in solution as a THF adduct. During electrolysis, dendritic material was deposited on the platinum counter electrode. This material was collected and determined to be Na_3AlH_6 and Al from X-ray diffraction (XRD) data.

Experiments were conducted to determine the feasibility of plating sodium at the platinum cathode to complete the cycle. The platinum cathode and aluminium anode potentials were -2.89 V and -1.31 V, respectively. Plating of Na metal was observed at the cathode while alane was produced at the aluminium anode. In this case, no dendrites were observed at the platinum cathode as sodium was reduced. Furthermore, bubbling hydrogen at the platinum cathode can form NaH and increase the efficiency by eliminating dendrite formation and the need to reduce Na^+ to sodium metal. With an over potential of ~ 0.3 V the alane process costs 25% of the value of H_2 stored in the alane. This value is less than that required in compression and liquefaction of H_2 gas (30–35%). Alane recovered from the electrochemical cells was characterized by powder XRD, Raman spectroscopy, and thermal gravimetric analysis (TGA). The methods of chemical separation and results of characterization are discussed herein. The separation of alane from the etherate adduct is well established and affords the pure AlH_3 compound. Separation of the $\text{AlH}_3 \cdot \text{THF}$ adduct is however not as straight forward as that of the etherate and has proven more sensitive to decomposition if isolated in the same manner as the etherate. For this reason we have explored the use of other adducts in purifying the product obtained from the cell. The procedure involves precipitation of the unconsumed sodium alanate using a non-polar hydrocarbon followed by filtration and introduction of triethylamine (TEA). The adduct free alane is then recovered by heating the neat liquid $\text{AlH}_3 \cdot \text{TEA}$ en vacuo.

XRD analysis was performed on a Bruker D8 system with Bragg-Brentano geometry, using Copper $\text{K}\alpha 1$ radiation and a NaI scintillation detector. Source voltage and tube current were 45 kV and 40 mA, respectively. Scans were performed using a 2θ range of 5 to 80 degrees with a step size of 0.02° and a scan speed of 1.0 seconds per step. Patterns were indexed with the Fullprof Suite of programs utilizing TREOR and DICVOL methods. Space group determination was performed using the program Chekcell. Powder XRD patterns data for two different separation methods are shown in Figure 2. When alane is separated by simply heating the $\text{AlH}_3 \cdot \text{THF}$ product after removing left over starting materials, the diffraction pattern shows the presence aluminum metal as well as α -alane. Separation using the TEA method affords only the pure α -alane phase as seen in the diffraction pattern; no aluminum is present. Indexing of this pattern was performed and

FIGURE 2. XRD patterns for products recovered from an electrochemical cell. (a) Alane separated from reaction mixture as the THF adducts. When heated under vacuum to remove THF, the solid partially decomposes, losing hydrogen and affording aluminium. (b) Alane is recovered using TEA.

the unrefined unit cell parameters were found to be $a = 4.446 \text{ \AA}$ and $c = 11.809 \text{ \AA}$. Based on the systematic absences, the space group was assigned as R-3c which is consistent with α -alane [16].

Raman spectra were obtained using a holographic spectrometer (HoloSpec, Kaiser Optical Systems) and charge-coupled device detector (DV420-BV-133, Andor, -55 C) with 532 nm excitation (Verdi, Coherent, Inc., 25 mW at sample). The wavelength response of the spectrometer was calibrated with a neon arc lamp; the intensity response was calibrated with a National Institute of Standards and Technology-traceable halogen lamp. Peak positions for a 50/50 acetonitrile/toluene mixture matched accepted values within $\pm 1 \text{ cm}^{-1}$. Spectra were obtained using a 180-degree backscattering geometry with a fiber optic imaging probe (MultiRxn, Kaiser Optical Systems, Inc., 5 mm focal length, ~ 200 micron spot size at focus). Samples were sealed inside glass vials under an inert atmosphere and measured outside containment. There was little evidence of sample decomposition at this laser power (see Figure 3).

As part of this work we found that $\text{AlH}_3 \cdot \text{TEDA}$ could be easily produced, using the electrochemical method reported here without the use of catalysts. Producing $\text{AlH}_3 \cdot \text{TEDA}$ was used as a mean to confirm the formation of AlH_3 molecules in the electrochemical

FIGURE 3. Raman spectrum of material isolated from an electrochemical cell showing α -phase alane.

FIGURE 4. TEDA is known to complex with AlH_3 , appearance of precipitate signals alane molecule formation.

cell. Although AlH_3 can not be separated from AlH_3 -TEDA it was selected because it precipitates as white solid and its formation can be observed visually (see Figure 4). The visual observation of the formation of relatively large quantities of TEDA- AlH_3 was good qualitative indication of the high rate of producing AlH_3 in electrochemical cell. The formation of AlH_3 -TEDA adduct indicates that a whole range of adducts could be formed, using the electrochemical route.

Thermal gravimetric analysis was conducted on a Netzsch TG-DTA 409 PC LXXX. The sample heating ramp was 2°C per minute while using an atmosphere of argon with a flow rate of $25\text{ cm}^3\cdot\text{s}^{-1}$.

Conclusions and Future Directions

This generation cycle of alane presented in this work provides a clean, facile route to a high capacity H_2 storage material alane, while avoiding unrecoverable thermodynamic costs. This work is anticipated to impact other fields including those of thin films, adduct based syntheses, and the recycling and regeneration of other materials. This work can be concluded as:

- Conducted systematic study to achieve a closed generation cycle of alane.

- Developed a methodology to confirm the generation of AlH_3 using this cycle.
- Succeeded in using this cycle to produce large quantities of AlH_3 -TEDA.
- Produced gram quantities of alane, electrochemically.
- Identified other solvents to be tried for more efficient separation process.
- Started working on the efficiency aspects of the cycle and will continue in the future.
- Identified other complex hydrides that can be regenerated in similar manner and will be tried in the near future.
- A closed system cell is assembled and will be used in the future for higher efficiency.
- Other solvents forming alane adducts will be tried for higher efficiency of separation.

Special Recognitions & Awards/Patents Issued

- Electrochemical process and production of novel complex hydrides, IPC8 Class: AC25B100FI USPC Class: 205477, patent pending.

FY 2009 Publications/Presentations

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IV.A.1g Fundamental Studies of Advanced High-Capacity, Reversible Metal Hydrides

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Contract Number: DE-FC36-05GO15063

Project Start Date: April 1, 2005
Project End Date: February 28, 2010

Objectives

The objective of this project is to develop a new class of reversible materials that have the potential to meet the DOE 2010 kinetic and system gravimetric storage capacity targets. Current investigations include:

- The investigation of the hydrogen storage properties of magnesium nano-confined in carbon aerogels.
- The study of novel, high hydrogen capacity, borohydrides that can be reversibly dehydrogenated at low temperatures.
- The development of a method for the hydrogenation of Al to alane, AlH_3 , and/or LiH/Al to LiAlH_4 at moderate pressures in non-conventional solvents.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) System Weight and Volume

- (E) Charging/Discharging Rates
- (J) Thermal management
- (P) Lack of Understanding of Hydrogen Physisorption and Chemisorption

Technical Targets

The work on this project is currently exclusively devoted to materials that have demonstrated available hydrogen capacities of 7-17 wt% hydrogen. We have developed a system of for the full reversible dehydrogenation of $\text{Mg}(\text{BH}_4)_2$ to MgB_2 that has shown a record, >12 wt% reversible hydrogen capacity but requires further development to meet kinetic performance targets within the target temperature. We have also developed a highly efficient method of the direct hydrogenation of LiH/Al to Ti-doped LiAlH_4 (7 wt% hydrogen capacity, rapid dehydrogenation at 120-150°C) at moderate pressure and room temperature that has been estimated to have a well-to-tank (WTT) energy efficiency that approaches 60% and thus meets U.S. DOE targets.

Accomplishments

Nano-Confined Mg in Carbon Aerogels

- Confirmed MgH_2 incorporation in aerogel by transmission electron microscopy (TEM) imaging, energy dispersive X-ray spectroscopy, and X-ray diffraction (XRD).
- Obtained 23 wt% MgH_2 loadings in carbon aerogels with larger pore sizes.
- Determined the rate of dehydrogenation at 252°C is >5 times faster than the initial rate found for ball milled MgH_2 and that it remains approximately the same over four cycles of dehydrogenation/rehydrogenation.
- Established that thermodynamics of the dehydrogenation of MgH_2 are not altered by nano-confinement.

Novel Borohydrides

- Achieved full, ~14 wt% re-hydrogenation of MgB_2 to $\text{Mg}(\text{BH}_4)_2$ through a high pressure method that avoids formation of highly stable, $\text{MgB}_{12}\text{H}_{12}$.
- Confirmed that the only major product of high pressure hydrogenation is $\text{Mg}(\text{BH}_4)_2$ by magic angle spinning (MAS) ^{11}B nuclear magnetic resonance (NMR) spectroscopy.

- Filed patent application for method for hydrogenation of MgB_2 to $\text{Mg}(\text{BH}_4)_2$.

Hydrogenation in Non-Conventional Solvents

- Developed a method for the room temperature, direct hydrogenation of Ti-doped LiH/Al in liquefied dimethyl ether under 100 bar of H_2 .
- Optimized synthesis process such that charged, Ti-doped LiAlH_4 is obtained in >95% yield.
- Determined the WTT energy efficiency our direct synthesis process approaches the 60% U.S. DOE target.
- Filed patent application for our direct synthesis process.

Introduction

The development of high capacity, hydrogen storage materials that can be recharged under moderate conditions is a key barrier to the realization of a hydrogen economy. Towards this goal, we are exploring new approaches for homogeneous incorporation of high hydrogen capacity metal hydrides into carbon aerogels. Intercalation into these nano-porous materials may change the thermodynamics and/or enhance the kinetics of the reversible hydrogenation thus bringing previously non-viable, metal hydrides such as MgH_2 into the realm of practical hydrogen storage materials.

We are also developing high hydrogen capacity borohydrides as hydrogen storage materials. Our initial focus was on anionic transition metal complexes. The anionic character of these compounds was found to result in an increased stability and a reduced volatility when compared to neutral transition metal borohydride complexes. However, in the course of our studies, we found a method whereby the fully reversible dehydrogenation $\text{Mg}(\text{BH}_4)_2$ to MgB_2 can be achieved. In consideration of the >14 wt% hydrogen that is potentially cyclable with this system, it has become the focus of our efforts on borohydrides.

The dehydrogenation of AlH_3 to Al gives 10 wt% H_2 . With additives, controllable dehydrogenation is possible at acceptable rates below 100°C. The low (<10 kJ/mol H_2) ΔH_{dehyd} mandates very high pressures for charging at ambient or higher temperatures. Supercritical fluids (SCFs) have different physical properties than gases. It has been found that requisite pressures hydrogenations are reduced in SCFs (i.e. hydrogenations of organic molecules and NaH/Al to NaAlH_4). In collaboration with the University of New Brunswick, we are developing new approaches utilizing supercritical fluids recharging AlH_3 .

We are also exploring the direct synthesis of LiAlH_4 in liquefied dimethyl ether, Me_2O . LiAlH_4 releases hydrogen according to the two reactions seen in equations 4 and 5. Although the second reaction is endothermic ($\Delta H = +25$ kJ/mol H_2), the first reaction

is exothermic ($\Delta H = -10$ kJ/mol H_2) [1]. Since entropic change is strongly positive for hydrogen release, the first reaction is thermodynamically irreversible under all practical conditions and it has been widely accepted that LiAlH_4 cannot be recharged and there have been no reports of its use for reversible hydrogen storage. However, the unfavorable thermodynamics of Eq. 4 may be altered by carrying out the reaction in solution, with the solvation of LiAlH_4 contributing to an (ideally) endothermic ΔH value. As early as 1963, Ashby *et al.* reported that a mixture of LiH and activated Al in THF or diglyme solvent reacted with 350 bar H_2 at 120°C to produce LiAlH_4 [2]. An improvement of the synthesis of the tetrahydrofuran (THF) adduct has recently achieved by researchers at Brookhaven National Laboratory by using Ti additives to significantly lower the required pressure and temperature [3]. A variation of this synthesis was previously reported by Ritter *et al.* in a procedure that involves the high-energy ball milling of a LiH/Al mixture under H_2 pressure in the presence of THF [4]. While the methods of both Ashby and Ritter result in the ultimate formation of LiAlH_4 from LiH, Al and H_2 , they are impractical because of the requirements of high temperature, high pressure, and/or mechanical energy during the synthesis as well as subsequent heating removal of the THF solvent (vacuum drying at 60°C for several hours). Ashby noted that it is very difficult to remove the final vestiges of THF. The prolonged baking *in vacuo* required to remove THF will necessarily compromise the integrity of a Ti-activated product. Clearly, the key to practically is the identification of a solvent that is sufficiently coordinating to support the nascent LiAlH_4 in the reaction environment, yet which is also volatile enough to be removed easily once it has served this purpose.

Approach

We have developed a novel approach for the intercalation of Mg in carbon aerogel materials. This procedure achieves high, cyclable magnesium loadings in carbon aerogels without host degradation. Since this method is performed at relatively low temperatures, the pore size of the aerogel material is preserved without degradation. The high loadings are allowing us to conduct highly reliable studies of the effects of nano-confinement on the kinetics and thermodynamics of the dehydrogenation of MgH_2 .

We have found that group I and II salts of anionic transition metal borohydride complexes have several improvements over neutral transition metal borohydrides: including higher (9-13 wt%) hydrogen content; reduced volatility; increase stability; and for some, complexes such as $\text{Na}_2\text{Zr}(\text{BH}_4)_6$, very low levels of diborane evolution during the dehydrogenation. Our studies are currently focused on determining whether the thermodynamic parameters of these complexes will allow them to undergo reversible dehydrogenation. In the course of these investigations we have found that that ball-milled mixtures of MgB_2 and catalytic additives undergo full hydrogenation to $\text{Mg}(\text{BH}_4)_2$ at high pressures. We are currently conducting detailed studies of the reversible dehydrogenation >12 wt% H_2 from $\text{Mg}(\text{BH}_4)_2$.

Our previous efforts have resulted in the development a SCF medium for the hydrogenation of Al that facilitates the hydrogenation of Al to AlH_3 in $\sim 5\%$ yield. Attempts to achieve higher yields by conducting the hydrogenation in alternative SCFs and utilizing variety initiator and catalysts are currently underway.

We are also exploring the synthesis of LiAlH_4 in liquefied Me_2O . Dimethyl ether should perform well as the solvent for this reaction since it is more polar and volatile than diethyl ether, it forms a strong complex with Li^+ , and it evaporates quickly at room temperature (boiling point = -24°C).

Results

Task 1. Characterization of the Active Titanium Species in Ti Doped NaAlH_4

This task has been completed.

Task 2. Spectroscopic Studies of Complex Hydrides

This task has been completed.

Task 3. Thermodynamic Properties of Complex Hydrides

This task has been completed.

Task 4. Kinetic Enhancement of “Thermodynamically Tuned” Binary Hydrides

Previously we reported high (9-16 wt%) MgH_2 loadings of carbon aerogel without host degradation are obtained using organometallic method. TEM imaging studies of our magnesium nano-confined aerogel have been completed in collaboration with the California Institute of Technology. These studies point to the nano-size of the Mg and MgH_2 particles. We also examined the effect of pore size of carbon scaffold materials on the MgH_2 loading. Results showed that higher MgH_2

loadings can be obtained with materials that have larger pore sizes (Table 1).

TABLE 1. Effect of Increasing Pore Size on MgH_2 Loading

Scaffold	Activated Carbon	13 nm Carbon Aerogel	25 nm Carbon Aerogel
Pore Size (nm)	<2	13	25
Pore Volume (cm^3/g)	0.58	0.80	1.38
MgH_2 Loading (wt%)	4.2	17	23

We have found that the rate of dehydrogenation of the nano-confined MgH_2 at 252°C is >5 times faster than the initial rate found for ball milled MgH_2 and comparable to those found for nano-confined MgH_2 in carbon aerogels that was prepared by alternative methods at HRL (Figure 1). We have also conducted comparative cycling studies of MgH_2 incorporated into aerogel granules and aerogel powder. Dehydrogenation was carried out at 325°C under vacuum and hydrogenation was performed under 9-13.5 MPa at 177 - 325°C for 6-20 hours. We found that with aerogel granules, the dehydrogenation rates remained approximately the same over four cycles and that they contained about 12 wt% reversible MgH_2 (Figures 2 and 3). Cycling tests of aerogel powder showed an obvious degradation of the dehydrogenation kinetics, and aggregation of Mg was observed.

To improve the kinetics of dehydrogenation and re-hydrogenation of the nano-confined MgH_2 we incorporated Ti-catalyst in the carbon aerogel. The Ti(0) catalyst was synthesized in situ through the reaction of $\text{TiCl}_4 \cdot 2\text{THF}$ with LiAlH_4 . We developed two procedures to carry out this synthesis. The first involved initial preparation of Ti(0) incorporated aerogel that was next loaded with MgBu_2 and finally hydrogenated to MgH_2 . The second procedure involved the reciprocal impregnation of Ti(0) into MgH_2 . We found that the

FIGURE 1. The rate of dehydrogenation at 252°C is >5 times faster than the initial rate found for ball milled MgH_2 .

FIGURE 2. Reversible dehydrogenation kinetics of Mg intercalated carbon aerogels through four cycles.

initially prepared materials containing Ti catalyst did not show any kinetic improvement. In fact, the amount of H_2 evolution actually decreased when compared to the material without the Ti species.

We have started measurements of pressure-composition isotherms to accurately determine if the thermodynamic properties of MgH_2 are changed upon nano-confinement. The equilibrium pressure of MgH_2 nano-confined in 13 nm aerogel at 250°C agrees with database value of 0.9 atm for bulk MgH_2 . This preliminary result indicates that the enthalpy of dehydrogenation of the nano-confined MgH_2 is 70 kJ/mol which is not significantly different than that of bulk MgH_2 .

Task 5. Synthesis and Evaluation of Novel Borohydrides

We have found that the alkali metal salts of anionic transition metal borohydride complexes such $LiMn(BH_4)_4$ undergo rapid dehydrogenation at moderate (<150°C) temperatures while evolving high (>3) wt% of hydrogen. In some cases, only very minor the amounts of the undesirable, diborane side product are produced. However, we have not found the dehydrogenation of any of these materials to be reversible. In order to see if the re-hydrogenation can be achieved even at high pressures, we conducted experiments in the range of 900 bar in collaboration with Sandia National Laboratories.

Experiments involving the attempted hydrogenation of various ball-milled mixtures alkali metal borides or hydrides; transition metal hydrides and borides; and catalytic additives proved unsuccessful. However, hydrogen uptake was found to occur in experiments with mixtures of MgB_2 ; transition metal hydrides; and catalytic additive. Analysis of the product mixture by XRD showed that the transition metal component was unreactive while the MgB_2 was hydrogenated to $Mg(BH_4)_2$. The same result was achieved when starting with ball-milled mixtures of MgB_2 and the catalytic additive at 400°C and 900 atm. A previous effort

FIGURE 3. The MgH_2 intercalated carbon aerogel contains about 12 wt% of reversible MgH_2 .

within the Metal Hydride Center of Excellence headed by researchers at General Electric showed $Mg(BH_4)_2$ undergoes stepwise dehydrogenation to give MgB_2 while releasing 14.8 wt% H_2 as seen in equations 1-3. Thermodynamic considerations indicate that it

should be possible to hydrogenate MgB_2 to $Mg(BH_4)_2$ at moderate temperatures and pressures. However, experimentally it has proven possible to reverse only the processes in equations 2 and 3 at temperatures lower than 500°C. It has been suggested that this is due to the high kinetic stabilization of $MgB_{12}H_{12}$. Thus our finding of full hydrogenation to $Mg(BH_4)_2$ is a breakthrough in the effort to develop this compound as a hydrogen storage material. We have also confirmed its identity by MAS¹¹B NMR spectroscopy. This analysis is very important as previous studies of the hydrogenation of MgB have found that the obtained $MgB_{12}H_{12}$ is amorphous and thus cannot be detected by XRD. By contrast, ¹¹B NMR is able to detect all boron-containing materials in the product mixture. As seen in Figure 4, only one major boron-containing product is observed. The chemical shift of -41 ppm allows its clear identification as $Mg(BH_4)_2$ as the shift exactly matches that which we have observed for an authentic sample of $Mg(BH_4)_2$. Only a very minor signal is observed for $MgB_{12}H_{12}$, at -24 ppm indicating that it represents <5% of the product mixture. It is not clear at this point if the high-pressure low-pressure reaction proceed by the same pathway. Thus the minor amount of $MgB_{12}H_{12}$ that was obtained could be either a small amount of an unreacted intermediate in the catalyzed dehydrogenation pathway or, alternatively, it could be a

FIGURE 4. MAS ^{11}B NMR $\text{MgB}_2 + 2 \text{ mol\%}$ additive hydrogenated under 950 bar at 400°C .

small amount of product resulting from the competing, standard uncatalyzed pathway.

As seen in Figure 5, thermal desorption of $\text{Mg}(\text{BH}_4)_2$ synthesized from high pressure hydrogenation of MgB_2 yields 11.5 wt% hydrogen. If the catalyst contribution to sample weight is not taken into consideration, 12.7 wt% hydrogen is realized, representing about 86% conversion of MgB_2 to $\text{Mg}(\text{BH}_4)_2$. XRD analysis of the synthesized product shows the presence of MgO , which contributes to the low weight percent hydrogen.

Task 6. Recharging of Light Metal Hydrides in Non-Conventional Media

A variety of alternative SCFs, initiators and catalysts were screened in attempts to improve the yield of AlH_3 from the hydrogenation of Al in SCFs. However, we have been unable to improve upon the ~5% (surface only?) yield we reported last year.

In a more promising development, we have found that LiAlH_4 can be synthesized in liquefied dimethyl ether (Me_2O) at room temperature from the hydrogenation of a mixture of LiH and Al in the presence of very low amounts of Ti catalyst (0.5-0.2 mol%). The method requires only moderate pressures of H_2 (80-100 bar). On completion of reaction, the volatile Me_2O solvent and excess H_2 are vented leaving only fine, dry Ti-doped LiAlH_4 that, as seen in Figure 6, can be clearly identified by XRD. We have found that improved yields are obtained upon lowering the Ti doping level. As seen in Figure 7, the amount of hydrogen obtained from the materials synthesized by our methods upon heating between 80 and 150°C dramatically increases as the doping level is decreased from 2.0 to 0.2 mol%. At the lower Ti loading a $>7 \text{ wt\%}$ H_2 is obtained which corresponds to a yield of ca. 95% [5]. Thus we have found a highly efficient method of the direct synthesis of LiAlH_4 at low pressure and room temperature. In further consideration that the energy for compression of Me_2O and H_2 is about 1/5

FIGURE 5. Thermal desorption curve for high pressure, direct synthesized $\text{Mg}(\text{BH}_4)_2$.

FIGURE 6. XRD patterns of LiAlH_4 samples: (a) International Centre for Diffraction Data[®] ref; (b) ball milled (2.0 mol% TiCl_3); (c) fully dehydrogenated (0.2 mol% TiCl_3); (d) rehydrogenated (2.0 mol% TiCl_3); (e) rehydrogenated (0.2 mol% TiCl_3).

that of H_2 and that LiAlH_4 has a high solubility in Me_2O , a preliminary analysis conducted at Argonne National Laboratory has indicated that WTT energy efficiency of our regeneration process is great than 60% and thus in line with U.S. DOE targets.

Conclusions

In summary, using our low temperature, “neat organometallic” method, we have achieved high, 9-16 wt% Mg loadings in carbon aerogels without host degradation. Higher MgH_2 loadings obtained with

FIGURE 7. Temperature-programmed desorption plots for LiAlH_4 samples: (a) as-received; (b) ball milled with 2.0 mol% TiCl_3 ; (c) rehydrogenated (2.0 mol% TiCl_3); (d) rehydrogenated (1.0 mol% TiCl_3); (e) rehydrogenated (0.5 mol% TiCl_3); and (f) rehydrogenated (0.2 mol% TiCl_3).

materials that have larger pore sizes. In addition, our studies have concluded that nano-confinement of MgH_2 improves the dehydrogenation kinetics, but does not appear to effect its thermodynamic properties, most notably, the enthalpy of dehydrogenation.

We have also achieved the full re-hydrogenation of MgB_2 to $\text{Mg}(\text{BH}_4)_2$ through a high pressure method that avoids formation of highly stable, $\text{MgB}_{12}\text{H}_{12}$ that typically precludes a full, 14 wt% hydrogenation. This result was first indicted by XRD and also confirmed by MAS ^{11}B NMR spectroscopy studies which show that the only major product of the hydrogenation is $\text{Mg}(\text{BH}_4)_2$.

Finally, we have developed a method whereby 95% yields of fully charged, Ti-doped LiAlH_4 are obtained from the direct hydrogenation of Ti-doped LiH/Al . The method involves room temperature hydrogenation in liquefied dimethyl ether under 100 bar of H_2 . The WTT energy efficiency of a LiAlH_4 -based hydrogen system utilizing liquid dimethyl ether as a re-hydrogenation medium approaches the 60% US DOE target.

Future Directions

Nano-confined Mg in Carbon Aerogels

- Determining dehydrogenation and re-hydrogenation kinetics of aerogels loaded with both MgH_2 and Ti-catalyst.
- Obtain pressure-concentration-temperature isotherms to confirm nano-confinement has no effect on the ΔH_{dehyd} of MgH_2 .

Anionic Borohydrides

- Exploring variations in reactions conditions to improve yield of lower pressure, full hydrogenation of MgB_2 to $\text{Mg}(\text{BH}_4)_2$.
- Continue studies of the catalyzed and un-catalyzed hydrogenation of MgB_2 utilizing MAS ^{11}B NMR to determine the mechanism in order to improve kinetics.

Hydrogenation in Non-Conventional Solvents

- Maximizing the extended cycling capacity of Ti-doped LiAlH_4 through variation of the dopant concentration and recharging conditions in liquid Me_2O .
- Further detailed evaluation of WTT energy efficiency of the direct synthesis of LiAlH_4 in liquid in collaboration with Argonne National Laboratory.
- Continuing exploration of improving levels of hydrogenation of alane using alternative SCFs and variety of initiators/catalysts.
- Exploring SCF synthesis of $\text{Mg}(\text{AlH}_4)_2$.

Patent Applications

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2. "Reversible Hydrogen Storage with Magnesium Borohydride." Eva Ronnebro, Godwin Severa, and Craig M. Jensen, U.S. Patent Application 61/093,937, filed 11/08.

FY 2009 Publications/Presentations

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1. "Synthesis and Hydrogen Storage Properties of MgH_2 Incorporated Carbon Aerogel Scaffold." S. Zhang, A.F. Gross, S.L. Van Atta, M. Lopez, P. Liu, C.C. Ahn, J.J. Vajo and C.M. Jensen; *Nanotechnology* **2009**, *20*, 204005. nvited contribution for issue on Nanoscale Phenomena in Hydrogen Storage).
2. "Nanostructure Observations of AlH_3 during Dehydriding Reaction." K. Ikeda, S. Muto, I.K. Tatsumi, M. Mejo, S. Kato, M. Biemann, A. Zuttel, C.M. Jensen and S. Orimo; *Nanotechnology* **2009**, *20*, 204004. (invited contribution for special issue on Nanoscale Phenomena in Hydrogen Storage).
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Presentations

1. “Novel Borohydrides for Hydrogen Storage Materials”, International Energy Agency, Task 22, Hydrogen Storage Experts Workshop; Rome, Italy, October 6–10, 2009.
2. “High Pressure Hydrogenation of Magnesium Boride to Magnesium Borohydride at Moderate Temperatures”, Study of Matter under Extreme Conditions 2009, High Pressure Society of America, Western Caribbean, March 28 – April 3, 2009.
3. “Novel Borohydrides for Hydrogen Storage Materials” International Energy Agency, Task 22, Hydrogen Storage Experts Workshop; JejuIsland, Korea, April 19–23, 2009.

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IV.A.1h First-Principles Modeling of Hydrogen Storage in Metal Hydride Systems

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Contract Number: DE-FC36-05GO15066

Subcontractor:
David S. Sholl, Georgia Institute of Technology,
Atlanta, GA

Project Start Date: March 1, 2005
Project End Date: February 28, 2010

- Specific energy: 1.5 kWh/kg
- Energy density: 0.9 kWh/L

Accomplishments

- Performed density functional theory (DFT) to predict the equilibrium crystal shape of seven metals and their hydrides via the Wulff construction.
- Computed the contribution to the thermodynamics of metal hydrides from surface energies of nanoparticles.
- Computed the change in temperature required to produce a pressure of H_2 of 1 bar upon desorption due to surface energies of nanoparticles.
- Calculated the structures and energetics of on the order of 100 different configurations of $MgB_{12}H_{12}$ and $CaB_{12}H_{12}$.
- Generated simulated X-ray diffraction patterns for these materials and performed a Boltzmann averaging of the structures.
- Generated energy histograms of energetics of $MgB_{12}H_{12}$ and $CaB_{12}H_{12}$.
- Investigated the energetics of poisoning of LiH, NaH, and KH surfaces by oxygen and water.
- Computed reaction pathways and energy barriers for H_2O dissociation on LiH, NaH, and KH surfaces.

Objectives

- Compute thermodynamics of metal hydride systems.
- Compute interfacial properties of hydrides.
- Address fundamental processes in hydrogenation.

Technical Barriers

This project addresses the following technical barriers from the Storage section (3.3.4) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) System Weight and Volume
- (E) Charging/Discharging Rates (kinetics)
- (P) Lack of Understanding of Hydrogen Physisorption and Chemisorption

Technical Targets

This project is involved with developing new complex metal hydride materials that meet the DOE 2010 hydrogen storage targets:

Introduction

Complex metal hydrides such as alanates, amides and borohydrides of period 2 and 3 metals are promising materials for reaching high gravimetric and volumetric hydrogen densities for on-board fuel cell storage. A serious thermodynamic limitation of these materials is that high temperatures are often required to release H_2 . The reaction free energy for decomposition of practical materials must lie in a narrow range of values to allow reversible hydrogenation and dehydrogenation at acceptable temperatures and pressures. In addition, the kinetics of hydrogenation and dehydrogenation must be acceptable.

Approach

We use quantum mechanical methods for computing the structural, electronic, energetic, and kinetic properties of complex hydrides and related materials. The specific method we use for most of our calculations

is periodic plane wave DFT, which is an approach for computing the approximate solution to the Schrödinger equation for condensed phase (solids) materials. This method requires as input at least an initial guess for the crystal structure of material to be modeled. The DFT method can then be used to optimize the atomic coordinates of each atom in the unit cell, the volume, and the shape of the unit cell. More importantly, we have developed a DFT-based method that can be used to quickly and reliably estimate the enthalpies of reaction for complex hydrides. We have used this method to screen over 300 possible hydrogen storage reactions and have identified several promising materials that have not previously been investigated. We can also calculate the free energies of reaction, including computing the entropic contributions through the phonon density of states. This is a much more computationally demanding approach – we have performed such calculations for a subset of the most promising reaction schemes identified from our screening calculations. We have also used DFT methods to compute kinetics for surface reactions as an initial approach for studying kinetics of reactions involving complex hydrides.

We have used the Vienna Ab initio Simulation Package (VASP) to perform most of the calculations in our work. We have used the gradient corrected approximation with the Perdew-Wang 91 functional. We have used both ultrasoft pseudopotentials and the projector augmented wave method.

Results

A useful way to characterize the thermodynamics of hydrogen release or uptake by metal hydrides is to determine the temperature at which the metal hydride is in equilibrium with the metal when the H_2 pressure is 1 bar [1]. Under these conditions the free energy, or equivalently, the grand potential, of the two systems are equal [2]. For bulk samples, the grand potential can be estimated using DFT calculations by

$$\Omega(T) = E - \frac{1}{2}(E_{H_2} + E_{ZPE,H_2} + \tilde{\mu}_{H_2})n^H \quad (1)$$

where E is the total energy for the solid of interest computed from DFT, the quantities inside the parentheses are the energy, zero point energy (ZPE), and chemical potential of molecular H_2 , and n^H is the number of H atoms per metal atom in the solid [3-5]. This expression neglects ZPE in the solid and temperature dependent vibrational contributions to the solid's free energy; we return to these approximations below. From this expression for the grand potential, it follows that the bulk metal hydride and metal are in equilibrium when

$$\tilde{\mu}_{H_2}(T, P_{H_2} = 1 \text{ bar}) = \beta = \frac{2}{n^H}(E_{MH}^{bulk} - E_M^{bulk}) - (E_{H_2} + E_{ZPE,H_2}) \quad (2)$$

Here, MH and M denote the metal hydride and metal, respectively. To extend this expression to solid particles of finite size, the influence of surface energy on the overall energy of the solids must be included. Using quantities accessible via DFT calculations based on slab geometries, the surface energy is

$$\gamma = [E^{slab} - NE^{bulk}] / A \quad (3)$$

where E^{slab} is the total energy of the slab containing N metal atoms, E^{bulk} is the total energy of the bulk material per metal atom, and A is the total surface area exposed by both sides of the slab [6-8]. Here, the slab energy is defined using a slab that has been geometry optimized to include the effects of surface relaxation. Nanoparticles of a metal and its metal hydride are in equilibrium when

$$\tilde{\mu}_{H_2}(T, P_{H_2} = 1 \text{ bar}) = \beta + \alpha / N, \quad (4)$$

where

$$\alpha = \frac{2}{n^H} \left(\sum_i (A_{MH,i}^{surf} \gamma_{MH,i}^{surf}) - \sum_j (A_{M,j}^{surf} \gamma_{M,j}^{surf}) \right) = \frac{2}{n^H} \Delta(A^{surf} \gamma^{surf}) \quad (5)$$

The summations are necessary here to allow for particles that expose multiple surfaces. Once $\tilde{\mu}_{H_2}(T, P_{H_2})$ is known from either Eq. (2) or (5), the temperature at which the metal and metal hydride are in equilibrium, T_{eq} , is defined. In calculating T_{eq} , we assume that H_2 is an ideal gas.

An alternative way to describe the thermodynamic effects of nanosizing is to use the change in enthalpy between the reaction involving a nanoparticle and the reaction for the bulk materials,

$$\Delta\Delta H = \Delta H(N) - \Delta H(\infty) \quad (6)$$

In terms of the quantities defined above, this enthalpy change is simply

$$\Delta\Delta H = -\frac{\alpha}{N} \quad (7)$$

To make use of the formalism above, we need to determine the areas and surface energies of the surfaces exposed by each nanoparticle of interest. If the surface energies of each possible surface are known, the Wulff construction can be used to predict the equilibrium crystal shape (ECS) of the material [6,7,9]. To apply the Wulff construction, we used DFT to calculate the surface energy of each low index surface of seven elemental metals and their hydrides, as summarized in Table 1. A convenient feature of these low index surfaces for all the hydrides we considered is that each layer normal to the surface has the same stoichiometry as the bulk hydride. This means that there is no ambiguity in defining the termination of these surfaces [10].

Using the surface energies calculated from DFT, we applied the Wulff construction for the seven metals and metal hydrides we considered. We examined five low

index surfaces for Sc, and all of these surfaces appear on the ECS, with the (1011) and (1021) surfaces defining about 70% of the entire surface area. The (1020) surface is predicted to only account for 0.4% of the particle's total surface area. The same set of five surfaces was considered for Ti. For Ti, only four surfaces feature on the ECS, and the (1021) surfaces defines about half of the total surface area. Our calculated surface energies for Ti differ in several respects from the values reported by Wang, Zhang, and Xu using calculations with the modified embedded atom method (MEAM) [11]. For example, our calculations indicate that the (1021) surface has the lowest surface energy, while Wang et al.'s calculations suggested that the (1020) surface has a lower surface energy than (1021). Although DFT calculations do not give exact results for surface energies, it seems likely that our DFT results are more reliable than results from the semi-empirical MEAM. The ECS of ScH_2 and TiH_2 are much simpler than their metal counterparts, an observation that can be understood by noting that the partially ionic nature of these materials makes their surface energies much more anisotropic than the surface energies of elemental metals. These hydrides have only (111) surfaces on their ECS. The contribution of each surface to the total surface area on the ECS of each of the seven metals and hydrides we have considered is summarized in Table 1.

From the calculated surface energies and ECS, we used Eq. (5) to describe the influence on particle size on the thermodynamics of hydrogen evolution. Our results are summarized in Figure 1, which shows the difference between the equilibrium temperature, T_{eq} , for

a nanoparticle and a bulk material. In this figure, the size of the metallic nanoparticle is shown by converting the volume of the nanoparticle with the predicted Wulff ECS to a spherical particle with the same bulk density. The numerical values of α for each metal/metal hydride pair are defined in Table 2 by listing $\alpha N^{-2/3}$, a quantity that is independent of N . An initial observation from Figure 1 and Table 2 is that both positive and negative deviations of the transition temperature with respect to the bulk material exist. For MgH_2/Mg and NaH/Na , the sign of α is positive, so the transition temperature decreases as the particle size is reduced. The opposite trend is seen for the other five metal/metal hydride pairs.

A second observation from Figure 1 is that the changes in the transition temperature relative to the bulk materials are, on the whole, small. For metal particles with radius 10 nm, the effects from the exposed surfaces change the transition temperature by less than 20 K for every material. For the two cases where the transition temperature is lower for nanoparticles than for the bulk material, the temperature is only reduced by 33 (16) K for MgH_2/Mg (NaH/Na) for the extreme case of a nanoparticle having a radius of 1 nm. The largest effect of nanoparticle size is predicted for VH_2/V . If we consider a V nanoparticle with radius 5 nm as an example, the transition temperature in this case is only 30 K larger than for the bulk system. We note that for most systems it is desirable to reduce the transition temperature or heat of reaction. However, for AlH_3 , it would be useful to increase the transition temperature (or equivalently, the heat of reaction) because at equilibrium, AlH_3 decomposes at temperatures that are

TABLE 1. Summary of the surfaces examined for each material in applying the Wulff construction to form the ECS. The final column indicates the fraction of the total surface area on the ECS associated with each surface.

Space group	Material(s)	Surfaces examined	Surfaces on ECS
$\text{Im } \bar{3}\text{m}$	V	(111), (110), (100)	(110) – 70%, (100) – 24%, (111) – 6%
	Li	(111), (110), (100)	(110) – 53%, (100) – 39.3%, (111) – 7.7%
	Na	(111), (110), (100)	(110) – 78.1%, (100) – 21.2%, (111) – 0.7%
$\text{P6}_3/\text{mmc}$	Sc	(0001), (10 $\bar{1}$ 0), (10 $\bar{1}$ 1), (11 $\bar{2}$ 0), (11 $\bar{2}$ 1)	(10 $\bar{1}$ 1) – 38.7%, (11 $\bar{2}$ 1) – 33%, (0001) – 15.8%, (10 $\bar{1}$ 0) – 12.1%, (11 $\bar{2}$ 0) – 0.4%
	Ti	(0001), (10 $\bar{1}$ 0), (10 $\bar{1}$ 1), (11 $\bar{2}$ 0), (11 $\bar{2}$ 1)	(11 $\bar{2}$ 1) – 55.5%, (10 $\bar{1}$ 1) – 24.5%, (0001) – 17.2%, (10 $\bar{1}$ 0) – 2.8%
	Mg	(0001), (10 $\bar{1}$ 0), (10 $\bar{1}$ 1), (11 $\bar{2}$ 0), (11 $\bar{2}$ 1)	(10 $\bar{1}$ 1) – 38%, (10 $\bar{1}$ 0) – 37.8%, (0001) – 24.2%
$\text{Fm } \bar{3}\text{m}$	Al	(111), (110), (100)	(111) – 75.5%, (100) – 24.5%
$\text{Fm } \bar{3}\text{m}$	VH_2	(111), (110), (100)	(111) – 100%
	LiH	(111), (110), (100)	(100) – 100%

FIGURE 1. The variation in the metal/metal hydride transition temperature relative to the result for a bulk material determined as described in the text.

too low for practical applications [12]. The nanoparticle transition temperature does indeed increase for the AlH_3/Al system, as seen in Figure 1, but the effect is extremely small, increasing T_{eq} by only 13 K for the extreme case of a metal nanoparticle 1 nm in radius.

Our results are shown in Figure 2 in terms of the enthalpy instead of temperature. As has already been discussed by focusing on the transition temperatures for these materials, the enthalpy changes associated with even very small nanoparticles are small.

To consider the physical source of the trends in α listed in Table 2, we calculated the charge associated with the H atoms in each metal hydride we examined using a Bader charge decomposition [13]. The resulting charges are shown in Figure 3. With the exception of LiH, there is a distinct correlation between α and the H atom Bader charge in the hydride, with the most (least) ionic materials being associated with positive (negative) values of α .

TABLE 2. The numerical coefficient, α , that controls nanoparticle thermodynamic effects for the seven systems we have considered, where N is the number of metal atoms in the nanoparticle.

System	$\alpha/N^{2/3}$ (eV)
VH_2/V	-1.608
LiH/Li	-0.822
ScH_2/Sc	-0.667
TiH_2/Ti	-0.461
AlH_3/Al	-0.107
NaH/Na	0.134
MgH_2/Mg	0.296

FIGURE 2. The variation in the metal/metal hydride reaction enthalpy relative to the result for a bulk material determined as described in the text.

FIGURE 3. Plot of $\alpha/N^{2/3}$ as a function of the charge on the H atom in the bulk hydride as computed by Bader charge analysis, where α is the parameter that controls nanoparticle thermodynamic effects and N is the number of metal atoms in the nanoparticle. The line is a linear fit to all systems except LiH/Li.

Conclusions and Future Directions

- We have computed the effects of nanoparticle surface energies on the thermodynamics of hydride reactions. We have found that for the simple hydrides we tested that the effect of nanosizing is to increase the temperature required to generate one bar of H_2 pressure, which is just the opposite of the effect desired in most cases. Moreover, the change in temperature is typically very small.

- Our calculations on nanoparticles cannot explain the experimental results for complex hydrides confined in porous materials.
- We have studied the kinetics and of poisoning of metal hydride surfaces in an effort to explain the observed differences in reversibility for reactions involving $MH+Al$, for $M=Li, Na$, and K . We found that all three hydrides were readily poisoned by water and oxygen. However, poisoning of LiH by O was seen to form a surface $LiOH$ structure that is commensurate with the LiH lattice and very similar to the $LiOH$ bulk structure.
- We plan to finish up calculations of multiple step reactions and metastable reactions.
- We will publish a paper on the effects of amorphous closo-borane materials on the reversibility of borohydride compounds.

FY 2009 Publications/Presentations

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3. J. Karl Johnson, "Quantum and Statistical Mechanical Modeling of Adsorption, Transport, and Reactions at Surfaces", *Dynamics and Chemistry of Surfaces and Interface Basic Research Workshop* June 23–25, 2009, 700 Drayton Streetm, Savannah, GA, USA.
4. J. Karl Johnson, "Adsorption and diffusion of hydrogen in nanoporous materials", 237th ACS National Meeting, March 22–26, 2009 in Salt Lake City, Utah.
5. J. Karl Johnson, "Atomistic Modeling of Hydrogen Storage in Complex Metal Hydrides", University of Nebraska-Lincoln, Department of Chemistry Colloquium, February 13, 2009, Lincoln, NE.
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IV.A.1i Thermodynamically Tuned Nanophase Materials for Reversible Hydrogen Storage

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Technical Targets

Destabilized System	Benchmark	2008 Status	2008/09 Progress
$\text{LiBH}_4/\text{MgH}_2$ @C aerogel 11.4 wt%, 0.095 kg/L without aerogel, est. $T_{1\text{ bar}} = 170^\circ\text{C}$	Could meet updated 2015 system weight and volume capacity goals (assuming 25% aerogel and 35% system penalties)	For LiBH_4 @ C aerogel, reduced capacity penalty to 40% Measured 10x equilibrium pressure Incorporated Mg into aerogel Measured >60x reaction rate	Incorporated complete destabilized system into aerogel Reaction temperature lowered but with degradation Mesoporous carbon synthesized and shows promise for improved kinetics
$\text{LiBH}_4/\text{Mg}_2\text{NiH}_4$ 8.3 wt%, est. $T_{1\text{ bar}} = 150^\circ\text{C}$	Could meet updated 2015 system capacity goal (with 35% system penalty)	Reversible capacity of ~6.5% at 350°C Slight degradation observed	Measured $T_{1\text{ bar}}$ of 65°C for low temperature step Hydrogenation of ternary boride confirmed

Objectives

- To identify and test new high capacity Li- and Mg-based destabilized hydride systems:
 - Investigate involvement of ternary borides in the $\text{LiBH}_4/\text{Mg}_2\text{NiH}_4$ system.
 - Study the kinetics and thermodynamics of the $\text{LiBH}_4/\text{Mg}_2\text{NiH}_4$ system focusing on the low temperature dehydrogenation step.
- Explore use of nanoconfinement to improve the kinetics of complex hydrides:
 - Incorporate complete $\text{LiBH}_4/\text{MgH}_2$ destabilized system into carbon aerogel and characterize the hydrogen exchange kinetics.
 - Investigate effects of pore size and pore size distribution on reaction rates of LiBH_4 .

Technical Barriers

This project addresses the following technical barriers from the Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) System Weight and Volume
- (C) Efficiency
- (E) Charging and Discharge Rates

Accomplishments

- Investigated $\text{LiBH}_4/\text{Mg}_2\text{NiH}_4$ system:
 - Observed first kinetically destabilized system.
 - Confirmed the formation of ternary borides.
 - Synthesized ternary borides and observed their hydrogenation.
- Incorporated $\text{LiBH}_4/\text{MgH}_2$ destabilized system into scaffold:
 - Observed lower dehydrogenation temperature but with poor cycling.
 - Tentatively assigned poor cycling to poor mixing of components.
 - Developed synthetic capability of mesoporous carbon at HRL.
 - Observed effect of pore architecture on reaction rate.

Introduction

This project is developing solid-state materials consisting of light elements to meet the capacity goals set forth by the DOE for on-board vehicle hydrogen storage

systems. While many light element compounds are known to have high hydrogen storage capacities, most of these materials are too thermodynamically stable and, consequently, the temperatures for hydrogen delivery are too high. In addition, hydrogen exchange is often too slow for practical use. In this project we are developing new material systems that can deliver hydrogen at lower temperatures and at higher rates. These advancements are made possible by tuning the thermodynamics and kinetics of the hydrogenation/dehydrogenation reactions.

Approach

HRL's technical approach has two principal components: 1) hydride destabilization by alloy or compound formation in the dehydrogenated state is used to develop new chemical systems that overcome the thermodynamic constraints imposed by high bond energies in light metal systems, and 2) nano-engineering of reactants is utilized to reduce the effective diffusion distances and thereby increase the rate of hydrogen exchange.

The first component of our approach, hydride destabilization, is built upon the idea that if the dehydrogenation product of a light metal hydride can react with another material to form a more stable phase, the overall enthalpy of the reaction will be lowered, thereby decreasing the temperature for hydrogen exchange. The modified system can cycle between the hydride and the new stable phase instead of the pure metal. The thermodynamics of the reaction can be tuned with the use of materials that afford phases of different stability. Although the addition of a destabilizing agent imposes a gravimetric capacity penalty, it is possible to minimize this penalty by using metal hydrides or other light element compounds as destabilizing agents.

The second component of our approach addresses the kinetics limitations to hydrogen exchange reactions in light metal hydrides. We are using catalysts as well as nanoscale reactants to improve the overall reaction kinetics. Nanoscale reactants can reduce solid-state diffusion distances and their high surface/volume ratio can improve catalytic activity. In particular, we are investigating the use of nanoporous "scaffolds" as structure-directing agents for forming nanoscale metal hydride reactants. This approach has the additional advantage of mitigating potential problems that can arise from agglomeration and sintering of the nanostructured material during hydrogen cycling.

Results

There were two main objectives for this project in Fiscal Years 2008/2009: (1) evaluate the $\text{LiBH}_4/\text{Mg}_2\text{NiH}_4$ destabilized system developed in 2007/2008 to elucidate

its reaction mechanism, in particular, to clarify the role of ternary borides which could provide a new direction for hydrogen storage material discovery; and (2) incorporate the complete destabilized system of $\text{LiBH}_4/\text{MgH}_2$ into carbon aerogel scaffolds and evaluate the effect of nanoconfinement on reaction kinetics; continue to investigate the effects of pore size and pore size distribution of carbon scaffolds on hydrogen sorption kinetics.

In the previous year, we discovered and performed preliminary characterization of a new destabilized reaction between LiBH_4 and Mg_2NiH_4 . Nuclear magnetic resonance (NMR) and X-ray diffraction (XRD) studies of the dehydrogenation product revealed the formation of ternary borides although their exact identity was unknown due to identical XRD patterns for many ternary boride compounds. Work in this year focused on 1) characterization of a low temperature hydrogen desorption step that might indicate kinetic destabilization; 2) chemical synthesis of ternary borides and confirmation of their roles in hydrogenation; and 3) obtaining data on the reaction thermodynamics after the reaction is identified.

Kinetic Destabilization – In the well known destabilized system of $\text{LiBH}_4/\text{MgH}_2$, MgH_2 first dehydrogenates to form Mg which in turn reacts with LiBH_4 to form MgB_2 , LiH and hydrogen. Despite an estimated $T_{1\text{bar}}$ of 170°C , the reaction in reality does not take place until after the dehydrogenation of MgH_2 , which has a $T_{1\text{bar}}$ of 280°C . In other words, kinetic pathways prevent the realization of the full benefit of thermodynamic destabilization. In contrast, the $\text{LiBH}_4/\text{Mg}_2\text{NiH}_4$ system does not appear to go through this multi-step process. Figure 1 shows the hydrogen desorption profile of a $0.8\text{LiBH}_4/\text{Mg}_2\text{NiH}_4$ mixture into 4 bar of hydrogen overpressure. Also included for comparison are profiles for Mg_2NiH_4 desorption into 4 bar of hydrogen and LiBH_4 into vacuum. There

FIGURE 1. Dehydrogenation profiles of LiBH_4 into vacuum and Mg_2NiH_4 as well as a $0.8\text{LiBH}_4 + \text{Mg}_2\text{NiH}_4$ mixture into 4 bar of hydrogen overpressure. The low temperature step for the mixture is absent from either of the components.

are three distinct steps for the destabilized system. Of particular interest is the low temperature step between 250 and 325°C. This low temperature step does not occur for either Mg_2NiH_4 or LiBH_4 individually (dehydrogenation of LiBH_4 would have taken place at even higher temperature into 4 bar of hydrogen than into vacuum). This observation argues that the two components reacted directly prior to their own decomposition, i.e., this is a kinetically destabilized system. As far as we know, this is the first example of such a system. Its identification is important since kinetic destabilization is required to ever realize useful reaction rates at temperatures approaching the thermodynamic ($T_{1\text{bar}}$) value.

Reversible Hydrogenation of Ternary Borides

– Another important feature of the new destabilized reaction is the formation of ternary borides. In the previous year, XRD results confirmed their formation, but it was not possible to identify their exact composition, nor was it clear whether they were responsible for reversible hydrogen storage. In this year, by direct synthesis, we investigated potential ternary MgNi_xB_2 borides with $x = 0.5$ to 3. ^{11}B NMR results obtained by Sonjong Hwang at Caltech showed that single-phase compounds exist for $x = \sim 1.5$ to 3. In order to examine the hydrogenation of the ternary boride, a mixture of $\text{MgNi}_{2.5}\text{B}_2$, MgH_2 and LiH in the mole ratios of 1:4:2 was mechanically milled and hydrogenated at 300°C under 100 bar of hydrogen. Subsequent dehydrogenation was performed under 4 bar of hydrogen by ramping the temperature to 400°C. Calibrated ^{11}B NMR spectra (not shown) performed after hydrogenation indicated clearly that the ternary boride was participating in a reversible reaction to form LiBH_4 . In combination with hydrogen exchange reaction studies, the destabilized reaction is most likely the following:

Preliminary Thermodynamic Characterization

– Since lower reaction temperature was observed for the $\text{LiBH}_4/\text{Mg}_2\text{NiH}_4$ system, we proceeded to measure the thermodynamic properties of the system. Figure 2 shows the van't Hoff behavior for the system as compared to several other reversible complex hydride materials. A dehydrogenated mixture was hydrogenated at a given temperature and hydrogen overpressure and subsequently dehydrogenated. The hydrogenation overpressure was gradually raised until hydrogen uptake was confirmed by release of hydrogen during the subsequent desorption. For example, after holding at 310°C for one day, no hydrogenation was observed for hydrogen pressures ranging from 10 to 75 bar. When the hydrogen pressure was raised to 100 bar, desorption showed 1.3 wt% of reversible hydrogen uptake which was similar to the uptake obtained at 350°C and 100 bar.

FIGURE 2. Preliminary results of van't Hoff plots for $0.8\text{LiBH}_4/\text{Mg}_2\text{NiH}_4$. Dehydrogenated mixtures were first hydrogenated at a given temperature under certain hydrogen overpressure followed by dehydrogenation. The hydrogen overpressure for hydrogenation was increased until hydrogen absorption was observed during subsequent dehydrogenation. Empty squares indicate no hydrogenation and filled squares indicate hydrogenation. van't Hoff plots for related compounds are also included for comparison.

This result indicates that the equilibrium pressure of hydrogen at 310°C is between 75 and 100 bar. A similar sequence was performed at 280°C. These preliminary results allowed us to establish an approximate van't Hoff plot. The reaction was found to have a ΔH value of 30 kJ/mol and a $T_{1\text{bar}}$ of 65°C. These values represent marked improvements over the $\text{LiBH}_4/\text{MgH}_2$ system with ΔH of 40.5 kJ/mol and $T_{1\text{bar}}$ of 170°C.

In summary, $\text{LiBH}_4/\text{Mg}_2\text{NiH}_4$ is the first known kinetically coupled destabilized system, forms a ternary boride during dehydrogenation, and exhibits low ΔH and $T_{1\text{bar}}$ values. Despite its limited reversible capacity of 2.5 wt%, these attributes point to a potential new direction for material discovery that involves ternary borides. Future work includes more complete assessment of the thermodynamics of the system as well as search of other systems of higher storage capacity.

Our second objective for the year focuses on further exploring the use of nanoconfinement in porous carbon scaffolds to improve the kinetics of hydrogen exchange reactions. In order to incorporate the $\text{LiBH}_4/\text{MgH}_2$ destabilized system in carbon aerogels, HRL has been working on the incorporation of MgH_2 since last year. Molten Mg was incorporated with a preloading of Ni in the aerogel to enhance wetting. Unfortunately, the high temperature process resulted in low Mg loading as well as non-negligible destruction of aerogel structure. Craig Jensen's group at the University of Hawaii (UH) recently developed a new synthetic procedure for MgH_2 using a reaction between hydrogen and dibutyl magnesium, which greatly facilitates MgH_2 incorporation into carbon aerogel at temperatures as low as 150°C. We measured the hydrogen exchange reaction rate of an $\text{MgH}_2@\text{C}$ sample and found its kinetics to be similar to the HRL sample prepared with the melt-in process. Equilibrium

pressure of the sample at 250°C was 0.36 bar, very similar to the reported bulk value of 0.4 bar, indicative of no thermodynamic effect due to nanoconfinement.

We used the MgH_2/C sample from UH and incorporated an appropriate amount of LiBH_4 to complete the destabilized system. The final sample was 19.9 wt% LiBH_4 , 12 wt% MgH_2 , and 68.1 wt% carbon. The molar ratio of LiBH_4 : MgH_2 was 1.96. Figure 3 shows its dehydrogenation profile as compared to a catalyzed ball milled bulk sample. The aerogel sample shows a much lower temperature for the onset of dehydrogenation (300 vs 350°C) with the transition between the two dehydrogenation steps less well defined. This reduction in dehydrogenation temperature demonstrates the expected benefit of nanoconfinement on the hydrogen exchange kinetics. Unfortunately, there is a significant degradation of hydrogen storage capacity for the 2nd and the 3rd cycles (results not shown). One possible explanation is that MgH_2 and LiBH_4 are not well mixed in the pores of the aerogel. In other words, they may occupy different pores of the aerogel and go through hydrogen exchange reactions separately. The reduction in the onset temperature of dehydrogenation is similar to what would be observed with a LiBH_4 loaded carbon aerogel. Since LiBH_4 is not fully reversible even when incorporated in the aerogel, the degradation in storage capacity would be expected. This hypothesis is supported by two additional observations: 1) the sum of the hydrogen desorption profiles of pure MgH_2 and pure LiBH_4 is very close to that of the combined system as also shown in Figure 3. The lower desorption temperature of the destabilized system can be attributed to the lower decomposition temperature of LiBH_4 in the aerogel; and 2) dehydrogenation products at 325°C, i.e., before MgH_2 decomposition occurs under 4 bar H_2 have no MgB_2 as confirmed by NMR analysis. This result further argues that the low temperature decomposition

step does not involve a coupled reaction between LiBH_4 and MgH_2 which would likely lead to the formation of MgB_2 . Work is in progress to develop synthetic method to enable simultaneous incorporation of both Mg and Li compounds in the aerogel to ensure uniform mixing.

We have also continued to evaluate additional carbon scaffolds in search of the maximum kinetic impact while minimizing the volume and weight penalty. Shown in Figure 4a are scanning electron microscope (SEM) images of three representative carbon materials with distinct microstructures. The mesoporous carbon synthesized from porous polymer (HRL meso-C) has long, straight but not interconnected pores while the mesoporous carbon synthesized by reverse casting from mesoporous silica has long, straight but interconnected pores. The carbon aerogel, on the other hand, has isotropic random pores. These differences in architecture have a direct impact on hydrogen desorption kinetics as shown in Figure 4b. HRL meso-C has an initial rate very similar to those of aerogel and the reverse cast mesoporous carbon. However, unlike all the other materials, its rate gradually decreases with time. We could explain these observations by attributing them to the effect of the one dimensional porous architecture. As the dehydrogenation proceeds the reaction products of LiH and B gradually accumulate in the pores which impede the release of hydrogen. In contrast, carbon aerogels and the reverse cast mesoporous carbon both have three dimensional porous architectures which would ensure continued hydrogen access. These results provide further evidence that porous architecture, in addition to pore size and pore volume, is an important factor in its effectiveness in kinetic enhancement.

Conclusions and Future Directions

The major conclusions from FY 2008/2009 are:

- The $\text{LiBH}_4/\text{Mg}_2\text{NiH}_4$ destabilized system is the first to exhibit kinetic destabilization. The reaction involves reversible hydrogen exchange with ternary borides. Preliminary thermodynamic characterization gives a ΔH of 30 kJ/mol and a $T_{1\text{bar}}$ of 65°C, two of the lowest values reported for any borohydride based hydrogen storage system;
- The complete destabilized system of $\text{LiBH}_4/\text{MgH}_2$ has been incorporated into carbon aerogels. It shows reduced dehydrogenation temperature but poor cycling stability. Poor mixing of the two hydrides in the nanopores is most likely the cause; and
- Pore architecture, in addition to pore size of carbon scaffold has a significant impact on hydrogen exchange reaction kinetics. Interconnectivity between the pores is important to maintain fast reaction rate.

FIGURE 3. Hydrogen desorption profiles of the $\text{LiBH}_4/\text{MgH}_2$ destabilized system, pure MgH_2 , and pure LiBH_4 in carbon aerogels with a peak pore size of 13 nm. The profile for the destabilized system is very similar to the sum of the profiles from the components. Also included for comparison is the profile for the bulk destabilized system.

FIGURE 4. (a) SEM images of mesoporous carbon synthesized from porous polymer (HRL meso-C) and reverse casting from mesoporous silica (by Lawrence Livermore National Laboratory, LLNL) and a carbon aerogel; (b) hydrogen desorption profiles for the carbon aerogel, HRL meso-C, and a mesoporous carbon from reverse casting prepared by the Pacific Northwest National Laboratory which is similar to the LLNL material.

Future directions are:

- Complete thermodynamic characterization of the $\text{LiBH}_4/\text{Mg}_2\text{NiH}_4$ system;
- Search for other destabilized systems involving ternary borides with higher capacities;
- Develop synthetic methods to achieve simultaneous incorporation of LiBH_4 and MgH_2 for improved mixing; characterize its hydrogen exchange reaction kinetics; and
- Continue to optimize carbon scaffold pore structure.

FY 2009 Publications/Presentations

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IV.A.1j Catalyzed Nano-Framework Stabilized High Density Reversible Hydrogen Storage Systems

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Subcontractors:

- Sandia National Laboratories, Livermore, CA and Albuquerque, NM
- Albemarle Corporation, Baton Rouge, LA

Project Start Date: July 1, 2007
Project End Date: July 1, 2010

Objectives

Design and synthesize hydride/nano-framework composites with a wider range of doped, functionalized and catalyzed framework chemistries to improve:

- Reversibility
- Desorption temperatures/kinetics - overly stable materials
- Instability at ambient temperature - unstable materials

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) System Weight and Volume
- (E) Charging and Discharging Rates
- (P) Lack of Understanding of Hydrogen Physisorption and Chemisorption

Technical Targets

This project is intended to improve material reversibility and kinetics through nano-confinement and surface chemistry. This approach provides a path to reversible high density H₂ storage systems meeting the DOE 2010 targets:

System Gravimetric Capacity:	1.5 kWh/kg
System Volumetric Capacity:	0.9 kWh/L
Charging/Discharging Rates (system fill time):	1.2 kg/min

Accomplishments

To advance the understanding of how nano-frameworks can enhance the performance of hydrogen storage media, a range of hydride/framework combinations and associated parameters has been investigated in the past year. The accomplishments include:

- Down-selected functionalized C and ZrO₂ as most suitable framework materials for future catalyzation investigations.
- Simulated the atomic mechanism for heterogeneously catalyzed H₂ dissociation and H transfer to kinetically facilitate rehydrogenation of Ca(BH₄)₂ dehydrogenation products.
- Obtained a decrease in H₂ desorption temperature of the stable borohydride Ca(BH₄)₂ incorporated in C aerogels by solution-based incorporation.
- Demonstrated high loading of NaTi(BH₄)₄ *ligand in SiO₂ aerogel and improved its stability in the aerogel.

Introduction

Current complex hydrides have yet to meet the 2010 DOE systems targets, presenting a continuing challenge for the discovery of high capacity, reversible hydrides. For example, metal borohydrides [M(BH₄)_n] have the potential to meet the targets, but some materials are unstable (such as those containing Ti, Al, or Sc cations) and decompose within minutes or days. Other metal borohydrides (such as those containing Li, Na, K or Ca cations) decompose at temperatures that are higher than what is desired for proton exchange membrane fuel cell integration and cannot be recharged with gaseous hydrogen at moderate pressures. Thus, there is a need to develop novel techniques that enable high

capacity that is maintained over numerous absorption/desorption cycles. The current project addresses this by incorporating complex metal hydrides, with a focus on borohydrides, into nano-scale frameworks of a low density, high surface area skeleton material to stabilize, catalyze, and control desorption product formation associated with such complex metal hydrides.

Approach

The project at United Technologies Research Center (UTRC) is being conducted in close collaboration with other researchers from the DOE Metal Hydride Center of Excellence. The UTRC, Sandia National Laboratories (SNL), and Albemarle Corporation teamed to develop nano-frameworks compatible with specific advanced hydrogen storage materials.

The team uses an iterative atomistic/thermodynamic modeling and experimental approach to develop hydride/nano-framework composites. The hydride/nano-framework interaction is chemically modified to decrease desorption temperature for highly stable compounds, stabilize unstable high capacity compounds, and influence desorption products to improve reversibility. In addition, nanometer-scale catalytic sites within the nano-framework cells will activate H_2 , and through hydrogen spillover, facilitate reversibility (rehydrogenation). Two high capacity borohydrides, $Ca(BH_4)_2$ and $NaTi(BH_4)_4$ were selected for incorporation into nano-frameworks. $Ca(BH_4)_2$ is a stable hydride that requires high temperature to desorb and reabsorb hydrogen. $NaTi(BH_4)_4$, however, is unstable and requires ligands to stabilize its structure. A variety of framework chemistries were examined to make a relatively broad assessment of the method's potential. These chemistries include functionalized, and catalyzed frameworks. Both melt and solution-based methods were employed for incorporation of hydride into nano-framework materials.

Results

In Fiscal Year 2009, much effort was devoted to examine chemical interactions of hydrides with a variety of nano-framework chemistries and their impact on the reversibility, hydride stability, and kinetics:

- Atomic Modeling:
 - Evaluated interaction of $Ca(BH_4)_2$ with ZrO_2 framework and its impact on $Ca(BH_4)_2$ dehydrogenation.
 - Investigated the effect of Pt catalyzed ZrO_2 on hydrogen dissociation and $Ca(BH_4)_2$ rehydrogenation.
- Framework and Hydride (Experimental):
 - Conducted evaluation of the reactivity of $Ca(BH_4)_2$ with oxides (Y_2O_3 stabilized ZrO_2

[YSZ], Al_2O_3 and SiO_2) and functionalized carbon aerogels.

- Identified the impact of uncatalyzed framework materials on $Ca(BH_4)_2$ rehydrogenation.
- Incorporated $Ca(BH_4)_2$ and $NaTi(BH_4)_4$ *DME (dimethoxyethane) in aerogels.

Atomic Modeling

1. $Ca(BH_4)_2$ * ZrO_2 Dehydrogenation

Atomic modeling was conducted to evaluate the impact of $Ca(BH_4)_2$ interactions with ZrO_2 frameworks on $Ca(BH_4)_2$ stability and dehydrogenation behavior. The simulations showed strong $Ca(BH_4)_2$ physisorption on the tetragonal $ZrO_2(101)$ surface, locally stabilizing $Ca(BH_4)_2$ at the interface. The simulations evaluated the various possible dehydrogenation reactions with the formation of adsorbed decomposition products. The strongest adsorbed product at the reacting interface was simulated to be CaH_2 . These model configurations are shown in Figure 1. The remaining products were assumed to be desorbed. When interfaced with ZrO_2 , the most accessible $Ca(BH_4)_2$ dehydrogenation reaction to form the CaH_2 , $CaB_{12}H_{12}$ and H_2 products was predicted to have an increased dehydrogenation enthalpy, where the increase was less than +20 kJ/m H_2 . This increase is barely distinguishable from the bulk $Ca(BH_4)_2$ reaction, taking typical calculation error into account. Other competing dehydrogenation reactions showed similar enthalpy increases and followed the same order of relative favorability, compared to bulk $Ca(BH_4)_2$. These simulations showed that the ZrO_2 framework characteristics need to be tuned to enhance $Ca(BH_4)_2$ reversibility.

FIGURE 1. Most favorable atomic modeling configurations of $Ca(BH_4)_2$ interface with tetragonal $ZrO_2(101)$ surface, in the fully hydrided (left) and dehydrided (right) states.

2. Pt Catalyzed Rehydrogenation

Atomic modeling investigations were made to demonstrate the utility of H_2 activation catalysts to facilitate the formation and transfer of atomic H, and enhance the binding and rehydrogenation of $Ca(BH_4)_2$ dehydrogenated phases. The H_2 activation catalysts were represented as 10 atom Pt nano-rafts anchored to the tetragonal $ZrO_2(101)$ surface. The results indicated that H_2 spontaneously dissociated on the Pt nano-raft, consistent with other reported experimental and theoretical findings. The transfer and migration of atomic H to adjacent ZrO_2 support were predicted to be favorable upon H saturation of the Pt nano-raft with increasing H_2 pressure during rehydrogenation. The presence of the Pt nano-raft enhanced the adsorption of $Ca(BH_4)_2$ dehydrogenation products on the surrounding ZrO_2 support. With increasing H_2 pressure, the simulations also showed spontaneous rehydrogenation of the dehydrogenation products adsorbed in the vicinity of the Pt nano-rafts. These predicted atomic configurations are shown in Figure 2. These results confirmed the feasibility and potential benefits for employing H_2 activation catalysts in hydrogen storage nano-frameworks.

Framework and Hydride (Experimental)

1. $Ca(BH_4)_2$ / Nano-Framework Interaction

Experiments were conducted to screen for undesired reactivity of $Ca(BH_4)_2$ with selected nanoscale oxides: SiO_2 , Al_2O_3 , ZrO_2 , and C aerogels: polyimide (PI) and phenolic (PF) derived carbon aerogels, using SPEX milled mixtures. This reactivity study was conducted to ensure the stability of the framework under cycling conditions. The experimental results indicated that ZrO_2 was the most stable oxide framework material under dehydrogenation at 350°C and 1 bar hydrogen

FIGURE 2. Atomic simulations of Pt nano-raft loaded on $ZrO_2(101)$ surface, showing spontaneous H_2 dissociation (left), atom H migration upon saturation (middle), and spontaneous rehydrogenation of co-adsorbed CaB_6 dehydrogenation product (right).

pressure and rehydrogenation at 350°C and 190 bar hydrogen pressure cycling conditions. SiO_2 and Al_2O_3 were susceptible to react with $Ca(BH_4)_2$ to form undesirable reaction products. No $Ca(BH_4)_2$ formed after rehydrogenation in the $Ca(BH_4)_2$ - ZrO_2 system, indicating that ZrO_2 inhibited $Ca(BH_4)_2$ formation. In $Ca(BH_4)_2$ - carbon (PI and PF derived) aerogel systems, formation of $Ca(BH_4)_2$ was observed upon rehydriding. No reaction products were observed in the $Ca(BH_4)_2$ - C (PF) system by X-ray diffraction analysis, while small amounts of $CaNH$ and Ca_3N_2 were detected in the $Ca(BH_4)_2$ - C (PI) system. Enhanced H_2 desorption was also observed in the SPEX milled $Ca(BH_4)_2$ - C systems compared with $Ca(BH_4)_2$ only. It was found that surface chemistry of the carbon aerogel affected kinetics of the second H_2 desorption after rehydriding. Based on these results, C aerogel was identified as the best uncatalyzed nano-framework material for $Ca(BH_4)_2$ incorporation. The effect of Pt catalyzed ZrO_2 nano-framework on $Ca(BH_4)_2$ rehydrogenation is currently under examination.

2. Incorporation of $Ca(BH_4)_2$ using Solution and Melting Methods

$Ca(BH_4)_2$ was incorporated into C aerogels using both solution and melting-based methods. Three solvated $Ca(BH_4)_2$ precursor species (adducts with tetrahydrofuran [THF], pyridine and dimethoxyethane [DME]) were synthesized and evaluated for incorporation via the solution method. The $Ca(BH_4)_2 \cdot THF$ precursor was pursued for incorporation in the C aerogel for its relative ease of desolvation. An estimated 27 wt% of $Ca(BH_4)_2$ was successfully incorporated in C (PI) aerogel. Brunauer-Emmett-Teller (BET) measurements showed that the surface area changed from 580 to 330 m^2/g after incorporation. The pore volume changed from 3.7 to 1.6 cm^3/g and the pore size from 25 to 19 nm. Preliminary testing using a Sievert's apparatus showed the on-set temperature for dehydrogenation decreased at least 50°C to 175°C. Its hydrogen release rate was improved significantly, compared with the SPEX milled $Ca(BH_4)_2$ - C (PI) system (Figure 3).

Incorporation of $Ca(BH_4)_2$ into carbon aerogel was explored via melting under high H_2 pressure and temperature. When a sample of $Ca(BH_4)_2$ and carbon (PI) aerogel was heated to 560°C under 10,000 psi of H_2 , it appeared that $Ca(BH_4)_2$ wetted the surface of the aerogel. However, the change in mass of the carbon aerogel was low, suggesting only minimal incorporation of $Ca(BH_4)_2$ within the pores. BET measurements showed a significant decrease in surface area from 400 to 2 m^2/g . The pore volume decreased from 2.5 to 0.02 cm^3/g . Hydrogen release behavior was measured using SNL's Simultaneous Thermo-gravimetric Modulated-Beam Mass Spectrometer (STMBMS) instrument. It was found that the H_2 release

FIGURE 3. H₂ desorption of Ca(BH₄)₂ incorporated in C aerogel, compared with SPEX milled Ca(BH₄)₂ and its mixture with C aerogel. (A) SPEX milled Ca(BH₄)₂, (B) SPEX milled mixture of Ca(BH₄)₂ with C (PI) aerogel, (C) Ca(BH₄)₂ incorporated in C(PI) aerogel at 27 wt% loading level.

temperature for the melt incorporated Ca(BH₄)₂ - C sample was higher than bulk uncatalyzed and catalyzed samples. The inability to achieve high sample loadings and the high H₂ releasing temperature have led to discontinuation of melt based method for incorporating Ca(BH₄)₂ into nano-frameworks.

3. Stabilization of NaTi(BH₄)₄*DME in SiO₂ Aerogel

NaTi(BH₄)₄*DME is a mixed alkali transition metal borohydride that was developed in a previous DOE contract (Complex Hydride Compounds with Enhanced Hydrogen Storage Capacity, DE-FC36-04GO14012) involving UTRC and the Albemarle Corporation. The complex is unstable at ambient temperature and decomposes within 1-2 days. In this project, NaTi(BH₄)₄*DME was incorporated into an oxide nano-framework to improve its stability. High surface area SiO₂ has been used as the nano-framework for the initial experiments. NaTi(BH₄)₄*3DME was used as the precursor for its high solubility in DME. Two levels of incorporation, 40 and 50 wt%, were achieved. After removing two portions of DME ligands, the loading levels became 26 and 34 wt% of NaTi(BH₄)₄*DME respectively. The stability of the incorporated material was improved from 1-2 days to >10 days at ambient temperature, as shown in diffuse reflectance infrared Fourier transform spectra (DRIFTS) of freshly made and aged NaTi(BH₄)₄*DME - SiO₂ composite (Figure 4). The improvement of stability was found to be more significant at the 26 wt% loading level than at 34 wt%.

FIGURE 4. DRIFTS of NaTi(BH₄)₄*3DME complexes incorporated in silica.

These results indicate that the hydride/nano-framework surface interaction helps to stabilize such unstable hydrides.

Conclusions and Future Directions

We have down-selected functionalized C and ZrO₂ as the most suitable framework materials. Atomic modeling indicated that Pt catalyzed zirconia aerogel can kinetically facilitate rehydrogenation of Ca(BH₄)₂. Ca(BH₄)₂ was successfully incorporated in C aerogels by solution method and its desorption kinetics were improved significantly. It was also demonstrated that SiO₂ aerogel can improve hydride stability of the unstable NaTi(BH₄)₄*DME.

Future Work

Atomic Modeling

- Design doped-ZrO₂ to balance interfacial interactions of hydrided and dehydrided storage material candidates.
- Survey influence of nano-framework surface functionalization on hydride/nano-framework interactions.

Framework and Hydride

- Evaluate the impact of Pt catalyzed ZrO₂ (YSZ) nano-frameworks.
- Examine stabilization effect of YSZ and C aerogels on the stability of NaTi(BH₄)₄*DME and removal of ligand.

- Consideration of alternate hydride candidates, such as $\text{Mg}(\text{BH}_4)_2$.

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IV.A.1k Neutron Characterization and Calphad in Support of the Metal Hydride Center of Excellence

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Project Start Date: April 1, 2005
Project End Date: October 1, 2009

Objectives

- Characterize structures, compositions, hydrogen dynamics, and absorption-site interaction potentials for candidate storage materials using neutron scattering methods.
- Provide Calphad calculations of phase relationships of potentially promising hydrides.

Technical Barriers

This project addresses the following technical barriers from the Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) System Weight and Volume
- (P) Lack of Understanding of Hydrogen Physisorption and Chemisorption

Technical Targets

We support the development of hydrogen-storage materials by providing timely, comprehensive characterization of Metal Hydride Center of Excellence (MHCoe)-developed materials and storage systems using state-of-the-art neutron methods and Calphad. This characterization helps speed the development and optimization of storage materials that can meet the following 2010 DOE hydrogen-storage system capacity targets:

- 6 wt% H
- 45 g H/l

Accomplishments

Key accomplishments for Fiscal Year 2009 are listed in the following for hydrogen-storage materials of interest to the MHCoe: (For more details, see the Results section.)

- The structures of $\text{Li}_2\text{B}_{12}\text{H}_{12}$, $\text{Na}_2\text{B}_{12}\text{H}_{12}$, and $\text{CaB}_{12}\text{H}_{12}$ were solved by a combination of X-ray diffraction (XRD), neutron vibrational spectroscopy (NVS), and density functional theory (DFT) calculations.
- NVS and nuclear magnetic resonance (NMR) data hint at the formation of a new $\text{Ca}(\text{AlH}_4)(\text{BH}_4)$ compound via ball-milling $\text{LiBH}_4 + \text{LiAlH}_4 + \text{CaCl}_2$.
- NVS and neutron prompt-gamma activation analysis (PGAA) indicate nontrivial amounts of sp^2 -bonded residual H in carbon aerogels.
- Confined $\text{Li}_3\text{BN}_2\text{H}_8$ in nanoporous carbon materials was shown to be partially reversible.
- Decreasing the filling of a 13 nm carbon aerogel with LiBH_4 increased the fraction that exhibited non-bulk-like BH_4^- reorientational dynamics.
- Neutron imaging techniques were shown to provide in situ, real-time diagnostics of practical hydrogen-storage beds.
- Neutron reflectivity measurements were found to be sensitive to the hydrogen profile formed within a single thin-film Mg layer during hydrogen cycling.
- The thermodynamic Calphad database for Li-Mg-Ca-B-Si-N-H was expanded to include more gas phase species and ternary hydride phases.

Introduction

In search of a hydrogen-storage medium that meets the DOE technical targets, the MHCoe has been investigating various materials, such as light-metal hydrides, borohydrides, and borohydride-amide mixtures. Moreover, considerable efforts have been focused on understanding the borohydrides' decomposition pathways in order to improve their hydrogen-cycling properties and enhance their reversibility. Using neutron-based probes, NIST has provided structural and/or spectroscopic

characterization of such materials as RbMgH_3 , RbCaH_3 , NaBH_4 , KBH_4 , $\text{LiK}(\text{BH}_4)_2$, $\text{Ca}(\text{BH}_4)_2$, $\text{Ca}(\text{AlH}_4)(\text{BH}_4)$, $\text{Li}_2\text{B}_{12}\text{H}_{12}$, $\text{Na}_2\text{B}_{12}\text{H}_{12}$, $\text{CaB}_{12}\text{H}_{12}$, $\text{MgB}_{12}\text{H}_{12} \cdot x\text{H}_2\text{O}$ and both LiBH_4 and $\text{Li}_3\text{BN}_2\text{H}_8$ nanoconfined in carbon aerogels. Such detailed information is important for a more thorough understanding of these materials and their hydrogen-storage properties. In addition, neutron reflectometry has been used to characterize hydrogen-concentration profiles within light-metal thin films during hydrogen cycling in order to understand the fundamental hydrogen diffusion mechanisms during hydrogenation and dehydrogenation. Finally, the usefulness of neutron imaging techniques has been explored for obtaining in situ, real-time diagnostics of practical hydrogen-storage beds.

Calphad thermodynamic modeling provides critical assessments of hydrogen content, character and heats of reaction, and phase-reaction sequences during hydrogen charge-discharge cycling of MHCoe-developed metal-hydride systems. NIST has continued to update and expand the thermodynamic database, including the elements Li, Mg, Ca, B, Si, N, and H and their respective binary and ternary phases, for the Calphad modeling of metal-hydrogen systems. This database is being used to calculate the reactions in multi-component hydrogen systems. These results are the basis for the evaluation of dehydrogenation temperatures and pressures and the suitability of element additions for destabilization of the hydride phases.

Approach

The key to improved hydrogen-storage materials is a detailed understanding of the atomic-scale locations and lattice interactions of the hydrogen. We are applying our state-of-the-art neutron measurement capabilities and expertise at the NIST Center for Neutron Research to the promising materials being developed by the MHCoe. This work enables MHCoe partners to obtain unique insights into the atomic- and molecular-scale properties that are responsible for the hydrogen-storage properties of these candidate materials.

In addition, we are performing Calphad thermodynamic modeling. The available literature is evaluated for thermodynamic data and analytical descriptions of the thermodynamic functions of the relevant phases. The data and functions are compiled into a consistent database describing the multi-component systems. Missing quantities are identified and descriptions are being developed in collaboration with MHCoe partners.

Results

We have focused the majority of our neutron measurements on borohydride-based materials in order to provide structural and spectroscopic details where

lacking. For example, we have collaborated with Sandia National Laboratories (SNL), Jet Propulsion Laboratory (JPL), Caltech, Maryland, and Missouri-Columbia to investigate the structures and bonding in the alkali and alkaline-earth dodecahydro-*closo*-dodecaborates, which are possible intermediates in borohydride decomposition. The structures of $\text{Li}_2\text{B}_{12}\text{H}_{12}$ ($P\bar{a}-3$), $\text{Na}_2\text{B}_{12}\text{H}_{12}$ ($P2_1/n$), and $\text{CaB}_{12}\text{H}_{12}$ ($C2/c$), were solved by a combination of XRD, NVS, and DFT calculations. The vibrational density of states associated with the $\text{B}_{12}\text{H}_{12}^{2-}$ anions proved to be sensitive to the crystal structure. For $\text{Li}_2\text{B}_{12}\text{H}_{12}$ (see Figure 1) [1], the Li^+ cation lies in a nearly trigonal planar site formed by three icosahedral $\text{B}_{12}\text{H}_{12}^{2-}$ anions, each of which resides in the octahedral cage defined by six Li^+ cations. Each $\text{B}_{12}\text{H}_{12}^{2-}$ anion orients two H atoms to each of the Li^+ cations, resulting in a strongly distorted octahedral coordination of the Li^+ cation with six H atoms. For $\text{Na}_2\text{B}_{12}\text{H}_{12}$ [2],

FIGURE 1. (top) The structure of $\text{Li}_2\text{B}_{12}\text{H}_{12}$ viewed along the (100) direction. The Li^+ cation position deviates from the ideal tetrahedral site (yellow ball) toward the near-trigonal-planar site along the body diagonal direction. (bottom left) Configuration of the six nearest Li^+ cations around the $\text{B}_{12}\text{H}_{12}^{2-}$ anion. (bottom right) Triangular arrangement of the $\text{B}_{12}\text{H}_{12}^{2-}$ anions surrounding a Li^+ cation. Li: red, B: green, H: silver.

each $B_{12}H_{12}^{2-}$ anion is surrounded by eight Na^+ cations, while each Na^+ cation interacts with four near-neighbor $B_{12}H_{12}^{2-}$ anions via nine H atoms. For $CaB_{12}H_{12}$, each Ca^{2+} cation is surrounded by five $B_{12}H_{12}^{2-}$ anions. Three $B_{12}H_{12}^{2-}$ anions form the triangular equatorial plane centered on each Ca^{2+} cation, while the other two $B_{12}H_{12}^{2-}$ anions are located in axial positions. Each Ca^{2+} cation interacts with eight neighboring H atoms from the five $B_{12}H_{12}^{2-}$ anions.

We have collaborated with SNL, JPL, Caltech, and Maryland to help characterize new MHCoE compounds such as novel borohydrides. $Ca(AlH_4)(BH_4)$ was predicted to be a potentially stable compound. Its possible synthesis via ball-milling of $LiAlH_4 + LiBH_4 + CaCl_2$ was studied by NVS and NMR. The resulting “amorphous” compound + LiCl indicated some spectroscopic similarities with $Ca(AlH_4)_2$, $Ca(BH_4)_2$, and $LiBH_4$, but clear differences exist. It appears that longer ball-milling times may be required to complete the reaction. Proper interpretation requires DFT phonon calculations, which are in progress.

We have collaborated with HRL Laboratories, Lawrence Livermore National Laboratory (LLNL), and Maryland to investigate the amount and nature of hydrogen in carbon-aerogel nanoscaffold materials. NVS and PGAA indicate nontrivial amounts of residual H (approaching ~ 0.1 H/C) in carbon aerogels, even after evacuation at 1,073 K. A typical spectrum (see Figure 2) reveals that the H is sp^2 -bonded to edge carbons, presumably as in coronene. We need to understand the effect of this H on the nanostructure of the aerogel as well as on the measurements and cycling properties of nanoconfined storage materials.

FIGURE 2. Typical Neutron Vibrational Spectrum of sp^2 -Bonded Hydrogen in 13 nm Carbon Aerogel at 4 K

We have collaborated with HRL, General Motors, Maryland, and Pennsylvania to study the effect of nanoconfinement on the cycling properties of $Li_3BN_2H_8$, which is a mixture of $(2/3)Li_4BN_3H_{10} + (1/3)LiBH_4$ with 11 wt% H and minimized NH_3 formation [3]. In contrast to the irreversibility of $Li_3BN_2H_8$ in bulk form, we have shown that its confinement in nanoporous carbon materials (*i.e.*, 13 nm carbon aerogel and 2 nm AX-21) renders it partially reversible. Moreover, a reduced desorption temperature occurs in the 2 nm AX-21 compared to in the 13 nm aerogel and in the bulk. Unfortunately, nanosequestration results in enhanced NH_3 formation, compared to the bulk, during dehydrogenation.

We have collaborated with HRL, LLNL, Maryland, and Michigan to study the effect of $LiBH_4$ fill fraction in carbon aerogels on BH_4^- dynamical properties. A comparison of $LiBH_4$ in 13 nm carbon aerogels (4% and 100% filled) was undertaken by quasielastic neutron scattering. The data suggest that partially-filled samples exhibit an increased fraction of $LiBH_4$ displaying faster, non-bulk-like BH_4^- reorientational dynamics. This may reflect preferential filling of smaller pores and/or surface film formation.

We have collaborated with JPL and Maryland to study the feasibility of using in situ neutron imaging techniques to map out the H distribution and transport in prototype hydrogen-storage beds, since such diagnostic tools are lacking. We simulated such a bed using an $LaNi_{4.78}Sn_{0.22}$ -based hydride compressor element identical to those used on JPL's Planck Sorption Cryocooler [4]. The $LaNi_{4.78}Sn_{0.22}$ powder was dispersed in a 10% dense Al foam in an annular bed geometry with an outer bed diameter of ≈ 3 cm. Hydrogen was added and removed through a central porous filter tube. Figure 3 displays some tomographic results using deuterium instead of hydrogen. Despite the non-uniform $LaNi_{4.78}Sn_{0.22}$ powder distribution, the D content of the filled bed is rather uniform. During desorption, D_2 preferentially escapes from the powder-depleted region, though this is likely due to the thermal control of the bed during desorption. (The heater does not reach to the end of the bed, and this cold region will be slower to desorb than the rest of the bed.) Such results confirm that the much lower total neutron cross section for D compared to H enables the probing of much thicker storage beds.

We have collaborated with Stanford and Maryland to help characterize hydrogen concentration profiles in thin Mg films. We have extended our measurements to a single (25 nm Pd-capped) 100 nm Mg layer on a sapphire substrate. Preliminary neutron reflectivity results before and after partially hydrogenating/dehydrogenating the Mg layer to different degrees indicate that the instrument is fully capable of determining the hydrogen profile through such a layer.

FIGURE 3. Sagittal slices through the tomographic reconstructions of the $\text{LaNi}_{4.78}\text{Sn}_{0.22}$ -based hydrogen-storage bed. The total attenuation coefficients of (a) the empty bed, (b) the bed filled with 100 L of D_2 , and (c) the bed after desorbing about 60 L of D_2 . In these images, black and white correspond to an attenuation coefficient of 0 cm^{-1} and 1.0 cm^{-1} , respectively. The large, open pore structure of the aluminum foam is clearly visible. Subtracting the empty bed attenuation coefficient yields the D content of the bed, which is shown in (d) after full absorption of about 100 L and (e) after desorption of about 60 L of D_2 .

The thermodynamic Calphad database has been updated and expanded. The original version of the thermodynamic database had six borane species in the gas phase. However, more borane gas-phase species are known to exist, and their thermodynamic description should be included in the database for accurate calculations of the gas phase. Thermodynamic quantities for 16 additional borane species were found in a literature search, and the thermodynamic functions for these species were evaluated and added to the database. Calculations with this expanded database showed that significant borane amounts occur only if no condensed phases with boron are present. The database has been further expanded to include descriptions for the solid phases $\text{Ca}(\text{BH}_4)_2$ (two polymorphs), $\text{CaB}_{12}\text{H}_{12}$, $\text{Mg}(\text{BH}_4)_2$, and amorphous boron. Experimental thermochemical data for amorphous boron were found in the literature and used for the development of the thermodynamic function. Experimental data for the ternary hydride phases are extremely sparse. Experimental data are available for the transformation temperature of the $\text{Ca}(\text{BH}_4)_2$ polymorphs and for the decomposition of the ternary hydride phases. For developing the thermodynamic descriptions of these phases, data from first-principles calculations provided by members of the Theory Group were used

FIGURE 4. Dehydrogenation Path of $\text{Ca}(\text{BH}_4)_2$ from Calculations using the Calphad Database

to supplement the experimental data. When available, heat capacity data were used from first-principles calculations. Otherwise, the heat capacity was obtained from the previously developed modification of the Neumann-Kopp rule. The phase descriptions were refined by adjusting them to the available reaction enthalpies and temperatures. The dehydrogenation path of $\text{Ca}(\text{BH}_4)_2$ is depicted in Figure 4. The path shows that the dehydrogenation occurs in two steps and that no solid elemental phases are formed during the dehydrogenation. Solid elemental phases, such as Ca, have a significant solubility for hydrogen and, therefore, can lower the amount of available hydrogen. The calculation also showed that the borane concentrations in the gas phase after dehydrogenation of the ternary phases is extremely small ($<10^{-8} \%$).

Conclusions and Future Directions

- Neutron methods and Calphad computations have provided crucial, non-destructive characterization and predictive tools for the MHCoe. We will continue these primary tasks in support of other MHCoe members.
- X-ray and neutron powder diffraction, neutron spectroscopy, and first-principles calculations provided a powerful combination for characterizing the structures and bonding of the dodecahydro-closo-dodecaborates. Spectroscopy was particularly useful to test predicted structures, even for “amorphous” samples. Work is still in progress to synthesize and characterize crystalline $\text{MgB}_{12}\text{H}_{12}$.

- We will continue to pursue the synthesis and characterization of a possible new hydrogen-storage compound, $\text{Ca}(\text{AlH}_4)(\text{BH}_4)$.
 - We will continue to investigate the importance of residual H in carbon aerogels on aerogel morphology and hydrogen cycling properties of nanosequestered storage materials by varying the aerogel pretreatment temperatures.
 - We will extend our studies of $\text{Li}_3\text{BN}_2\text{H}_8$ and similar materials in nanoporous carbons by investigating the role of catalyst dopants on hydrogen cycling kinetics, reversibility, and NH_3 formation.
 - We will continue to investigate the relationship between fill fraction and BH_4^- reorientational dynamics for LiBH_4 and NaBH_4 nanosequestered in carbon aerogels.
 - Feasibility studies of in situ neutron imaging of the H and D distribution and transport in a $\text{LaNi}_{4.78}\text{Sn}_{0.22}$ -based hydrogen-storage bed proved to be highly successful. This technique should greatly benefit the Engineering Center of Excellence to study prototype storage beds.
 - Neutron reflectivity was shown to be sensitive to the hydrogen density profile associated with a single, Pd-capped, 100 nm Mg layer on sapphire during the different stages of hydrogen cycling. Detailed analysis of the reflectivity data is in progress.
 - The thermodynamic database for Li-Mg-Ca-B-Si-N-H has been expanded to include more gas phase species, amorphous boron, and ternary hydride phases.
 - We will continue to expand the database to include more ternary hydride phase descriptions, e.g., $\text{MgB}_{12}\text{H}_{12}$, in collaboration with MHCoe partners.
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Special Recognitions

1. J.-H. Her was awarded 1st place in the 16th annual Postdoctoral Poster Competition sponsored by the NIST chapter of Sigma Xi, Gaithersburg, MD, Feb. 2009.

FY 2009 Publications/Presentations

1. J.-H. Her, M. Yousufuddin, W. Zhou, S.S. Jalisatgi, J.G. Kulleck, J.A. Zan, S.-J. Hwang, R.C. Bowman, Jr., and T.J. Udovic, "Crystal Structure of $\text{Li}_2\text{B}_{12}\text{H}_{12}$: a Possible Intermediate Species in the Decomposition of LiBH_4 ," *Inorg. Chem.* **47**, 9757 (2008).
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19. J.-H. Her, Y. Liu, C.M. Brown, M. Yousufuddin, T.J. Udovic, D.A. Neumann, A. Dailly, S.S. Kaye, J.R. Long, and S.S. Jalisatgi, "Structural Studies on Various Hydrogen Storage Materials: MIL-53, $K_2Zn_3[Fe(CN)_6]_2$ and $Li_2B_{12}H_{12}$," 16th annual Postdoctoral Poster Competition sponsored by the NIST chapter of Sigma Xi, Gaithersburg, MD, Feb. 2009.
20. U.R. Kattner, "A Thermodynamic Database for Laves Phase - Hydrogen Systems," CALPHAD XXXVIII, Prague, Czech Republic, May 2009.
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IV.A.1I Reversible Hydrogen Storage Materials – Structure, Chemistry, and Electronic Structure

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Project End Date: February 26, 2010

Technical Targets

This project is conducting fundamental experimental and theoretical studies of candidate lightweight systems for on-board regeneration. Insights gained from these studies will be applied toward the design and synthesis of hydrogen storage materials that meet the following DOE 2010 hydrogen storage targets:

- Cost: \$4/kWh net
- Specific energy: 1.5 kWh/kg
- Energy density: 0.9 kWh/L

Introduction

Our work at UIUC focuses on resolving issues within current hydrogen storage materials using a combination of electronic structure calculations and state-of-the-art compositional and structural characterization methods. We tie together theoretical understanding of electronic, enthalpic, thermodynamic, and surface effects affecting performance of storage materials with microcompositional and microstructural experimental analysis, coordinated with other efforts from MHCoe partners. These efforts enable a more efficient approach to designing a new system with the required properties.

Established partnerships in previous fiscal years with the following groups (Sandia National Laboratories [SNL], HRL, University of Pittsburgh (Pitt), Georgia Tech, and University of Hawaii). We expanded our collaborations to include Brookhaven National Laboratory. These partnerships have provided and will continue to produce meaningful results for the investigation of structure and chemistry for hydrogen storage materials.

Objectives

The main focus of UIUC within the Metal Hydride Center of Excellence (MHCoe) is:

- Advance the understanding of the microstructural and modeling characteristics of complex hydrides.
- Provide feedback and knowledge to partners within MHCoe framework.
- Provide more reliable theoretical methods to assess hydrogen-storage materials, including key issues affecting materials under study.

Technical Barriers

This project addresses the following technical barriers from the Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (E) Charging/Discharging Rates
- (P) Lack of Understanding of Hydrogen Physisorption and Chemisorption

Approach

We employ state-of-the-art characterization tools to investigate the microstructural and microchemical changes that occur in candidate material systems during the uptake and release of hydrogen. The characterization is coupled with first-principles, electronic-structure and thermodynamic theoretical techniques to predict and assess meta-stable and stable phases, as well as surface effects that can poison or limit kinetics. Electronic-structure and thermodynamic calculations are used to enhance the understanding of MHCoe experimental characterization results on

candidate systems. The theoretical work at UIUC is coordinated closely with MHCoE theory partners, as well as experimental efforts. This combined theoretical/characterization effort provides fundamental insight to the processes governing hydrogen uptake and release.

Results

Theory Efforts

We are continuing studies with several Center members. A selection of this work includes:

- Density functional theory studies of stability of intermediate phase in $\text{Ca}(\text{BH}_4)_2$ and $\text{Mg}(\text{BH}_4)_2$ systems (with SNL) are continuing. We have found a stable intermediate $\text{CaB}_{12}\text{H}_{12}$ closo-molecule, relative to segregation back to constituents used to obtain initial $\text{Ca}(\text{BH}_4)_2$ (with SNL). The reaction energies, summarized in Table 1, show that there are several (certainly more than have been found previously) near-degenerate structures, which is the origin of the irreversibility issues. A series of images showing different monoclinic unit cells of the material is shown in Figure 1. For the most stable structure (e), the space group is P2/m (No. 10). The lattice parameters of the base-centered monoclinic unit cell are $a=11.71 \text{ \AA}$, $b=7.02 \text{ \AA}$, $c=11.16 \text{ \AA}$ and $\beta=89.96^\circ$ (angle between a and c unit cell vectors). We have submitted for publication a paper that includes both the experimental and theoretical results that discusses why this system is irreversible.

TABLE 1. Reaction energies (product minus reactant) of dehydrogenation of $\text{Ca}(\text{BH}_4)_2$. Zero-point energies (bolded) are included in the top most values. Reaction 4 (with closo $\text{CaB}_{12}\text{H}_{12}$) is lowest in energy, while reaction 3 is lower per mol- H_2 . There are multiple related reactions of type 4 due to the importance of ionic charge, i.e. (a) NaCl-based monoclinic (C2/m); (b) distorted ZnS-type zinc-blende structure (P2); (c) disordered hcp Wurtzite structure (Pm); and (d) distorted hcp Wurtzite structure (C2/m); and (e) distorted hcp Wurtzite structure (P2/m).

	Reaction	$\Delta\text{H}(0 \text{ K})$	
		(eV)	(kJ/mol- H_2)
1	$\text{Ca}(\text{BH}_4)_2 \rightarrow \text{Ca} + 2\text{B} + 4\text{H}_2$	3.45	83.3
2	$\text{Ca}(\text{BH}_4)_2 \rightarrow \text{CaH}_2 + 2\text{B} + 3\text{H}_2$	1.80	57.8
3	$\text{Ca}(\text{BH}_4)_2 \rightarrow \frac{2}{3}\text{CaH}_2 + \frac{1}{3}\text{CaB}_6 + \frac{10}{3}\text{H}_2$	1.34	38.9
4	$\text{Ca}(\text{BH}_4)_2 \rightarrow \frac{5}{6}\text{CaH}_2 + \frac{1}{6}\text{CaB}_{12}\text{H}_{12} + \frac{13}{6}\text{H}_2$	--	--
4a	" (C2/m 50)	0.97	43.3
4b	" (P2 50)	0.92	41.2
4c	" (Pm 100)	0.90	39.9
4d	" (C2/m 100)	0.89	39.7
4e	" (P2/m 100)	0.88	39.4

FIGURE 1. Unit cells of $\text{CaB}_{12}\text{H}_{12}$ polymorphs. Labels refer to symmetry groups: (a) NaCl-based (C2/m); (b) distorted (zinc-blende) ZnS (P2); and four distorted Wurtzite with point-group symmetries of (c) Pm; (d) C2/m; (e) P2/m; and (f) P1.

- X-ray diffraction studies of desolvated and dehydrogenated $\text{Ca}(\text{BH}_4)_2$ samples obtained from SNL were performed to identify the phases present. Shown in Figure 2, the peaks for the desolvated $\text{Ca}(\text{BH}_4)_2$ phase matches well with those from the standard for $\alpha\text{-Ca}(\text{BH}_4)_2$ structure. After dehydrogenation, the $\text{Ca}(\text{BH}_4)_2$ peaks mostly disappear and new peaks, which match well with the standard CaH_2 pattern, appear. These X-ray diffraction results indicate that, save for CaH_2 , there are no identifiable crystalline intermediate phases present in the dehydrogenated samples. Electron diffraction from a single particle shows weak crystalline diffraction spots superimposed on a diffuse background. This pattern is consistent with the particle being amorphous with a low volume fraction of small crystalline regions. The diffraction pattern could not be identified which precluded identification of the crystalline material. Chemical analysis via electron energy loss spectroscopy, as noted in the previous report, confirms that there is no significant redistribution of the elements within the particle. Hence, the dehydrogenated intermediate phase is amorphous predominantly with no significant compositional modifications.
- In the $\text{CaB}_{12}\text{H}_{12}$ polymorphs, Figure 1, B is narrowly distributed inside the closo-molecule, yielding

FIGURE 2. X-ray diffraction patterns from desolvated and dehydrogenated $\text{Ca}(\text{BH}_4)_2$, with comparison to a standard (Fddd symmetry) from Miwa *et al* [1]. After background subtraction, modeled CaH_2 pattern matches closely with our dehydrogenated data. The few weak, unmatched peaks (e.g., $2\theta \sim 29^\circ$) do not fit to any Ca- or B-based compound, such as CaB_6 .

FIGURE 3. Nearest-neighbor Ca-Ca bond distributions for $\text{CaB}_{12}\text{H}_{12}$ in Figure 1, where (f) is similar to (d), but with rotated closomolecule units, showing the sensitivity of Ca-Ca bond distribution to closomolecule orientation.

a similar bond distribution for all polymorphs, with the only difference being in orientation. The largest difference is the positions of the Ca ions. The Ca-Ca bond-length distributions for these structures, Figure 3, varies from 5.5 Å to 7.6 Å. Since the structures are close in energy, multiple polymorphs are present, the competition of which leads to a broad distribution of Ca-Ca bond-lengths. Arrangement of the polymorphs such that there is no long-range order, coupled with the broad Ca-Ca

FIGURE 4. Formation enthalpy (kJ/mol) of CaB_xH_y versus δ (at% H_2) relative to (a) $\text{CaH}_2 + \text{B}$ and (b) $\text{CaH}_2 + \text{CaB}_6$. For $\text{CaB}_{12}\text{H}_{12}$ and $\text{Ca}(\text{BH}_4)_2$ δ in (a) is 5/17 and 3/5, and (b) 7/9 and 10/11, respectively. Dashed line indicates how much more stable $\text{CaB}_{12}\text{H}_{12}$ is relative to the constituent materials at each end of the line. Energies for $\text{CaB}_{12}\text{H}_{12}$ involve multiple structures (Figure 1) marked by “+” signs.

bond length provides a rationale explanation for the electron and X-ray diffraction data.

- Recent calculations, Figure 4, show that $\text{CaB}_{12}\text{H}_{12}$ is slightly lower in energy than a mixture of $\text{Ca}(\text{BH}_4)_2$ and $\text{CaB}_6 + \text{CaH}_2$. The energy barrier along the segregation pathway ($\text{CaB}_6 + \text{CaH}_2$) and the $\text{CaB}_{12}\text{H}_{12}$ intermediate state is much larger than that between $\text{CaB}_{12}\text{H}_{12}$ and $\text{Ca}(\text{BH}_4)_2$, indicating that the $\text{CaB}_{12}\text{H}_{12}$ intermediate phases are energetically favorable. The large chemical potential required to get back to “ $\text{CaH}_2 + \text{B} + \text{H}_2$ ” from $\text{CaB}_{12}\text{H}_{12}$, and similarly from $\text{Ca}(\text{BH}_4)_2$, inhibits reversibility, making the reverse reaction unlikely except at temperatures and pressure too high for practical use in hydrogen storage applications. Thus, $\text{Ca}(\text{BH}_4)_2$ has limited viability as a reversible storage material

for on-board storage for vehicles, but may still be promising as a chemical hydride.

Experimental Efforts

On the experimental side we continue to work with several of our partners. A selection of the work done includes:

- In conjunction with Brookhaven National Laboratory, we have investigated the location of the catalytic Ti in AlH_3 -triethylenediamine (TEDA). This material is the first hydrogen reversible alane produced and the results shown here are the first characterization results on this system. Through a combination of transmission electron microscopy and scanning electron microscopy (SEM), we have shown that large fibers exist and these show a strong aluminum and nitrogen peak, which is consistent with the formation of AlH_3 -TEDA. A representative image of these fibers is shown in Figure 5. In association with the fibers are occasional “bunches” of nodular particles which are composed primarily of Al, also indicated in Figure 5. These crystals are formed in solution with TEDA under hydrogen pressure.
- Within the nodular Al crystals, there is a high concentration of Ti that was not observed in the fibers. The AlH_3 -TEDA fibers have no detectable Ti, but the nodular crystals show Ti being present at a concentration of 0.4 at%. This stands in stark

FIGURE 5. Scanning electron microscope image of AlH_3 -TEDA (triethylenediamine) which has been doped with 0.1 mol % TiCl_3 . Within the large fibrous crystals, both Al and nitrogen are strongly identified, confirming that this material is the AlH_3 adduct described in Graetz *et al* [2]. This phase of material is formed in the liquid state under hydrogen pressure in a glovebox. Previously unknown small Al clusters or grains were also found in association with this material. These clusters were identified as essentially pure Al with 0.4 at % Ti. These clusters have high amounts of Ti with respect to how much was added to the material. This suggests that the TEDA is very selective for AlH_3 .

contrast to the doping concentration, which was 0.1 at% Ti. This result suggests that the Ti, when the material is placed under hydrogen pressure, assists the formation and departure of AlH_3 from the surface of the material. As soon as an AlH_3 molecule is formed at the surface, it is scavenged from the material and Ti is left behind. This result has implications for understanding the catalytic activity in NaAlH_4 and suggests that the action of Na is irrelevant and that the only important aspect is the interaction of Ti with the Al surface. In addition, the amount of Ti present in the remaining nodules is higher than that added, which means it has concentrated in the nodules. In conjunction with past research on the role of doping in NaAlH_4 , this suggests that much of the added Ti becomes inert or is lost. This result suggests that the amount of necessary titanium participating in the catalytic process is low and is <0.1 at%. Efforts are ongoing to identify partners who can provide low-temperature distillation to separate AlH_3 -ethylene diamine from the Al crystals for mass spectrometry to evaluate the Ti concentration necessary for catalysis.

- In collaboration with SNL, we are investigating the use of metal organic frameworks (MOF) as a medium to contain hydrogen storage materials. Theoretical proposals have suggested that making particles very small (<5 nm) may enhance the kinetics of hydrogen uptake and release from these storage materials. MOFs are porous, building-block structures with pore sizes on the order of a few nanometers. By infiltrating hydrogen storage material into MOFs, their particle size should be constrained by the pore sizes of the frameworks. There is a great need, however, to know where the hydrogen storage material is located within the MOF. That is, is the storage material on the surface or located within the MOF?
- Electron tomography reconstructions of both cured and uncured Ag-MOF systems were produced, Figure 6 and 7; this system was studied simply to demonstrate proof of concept. In both systems, the Ag particles were dispersed throughout the framework and not restricted to the surface. Nanowire structures were reported to be present in the uncured system, but their exact structure was unknown. From the reconstruction, Figure 8, it is obvious that the “nanowire” structure is neither extensive nor uniform, but has a morphology resembling a row of “sintered” Ag particles. The techniques used to visualize this material, of which a primitive form was previously demonstrated with Ni particles in MgH_2 , were advanced further during these experiments and now will be applied to hydrogen storage MOFs provided by SNL.

FIGURE 6. Tomographic reconstruction of a cured Ag-MOF specimen with contrast set to show (a) only the Ag particles, (b) only the framework, and (c) Ag and framework combined. The Ag particles are clearly spread throughout the inside of the MOF, not segregated to the surface.

FIGURE 7. Series of higher magnification images of the reconstruction of the cured Ag-MOF system from Figure 6 as it is being tilted. Relationship between the Ag particles and MOF is easily understood.

FIGURE 8. Tomographic reconstruction of an uncured Ag-MOF specimen with contrast set to show purported “nanowire” structures. The loss of depth information in 2-dimensional imaging led to confusion about actual structure of these wires, which is dispelled by the 3-dimensional reconstruction.

- Installation and calibration of new equipment for the variable temperature scanning tunneling microscope at the University of Illinois has been completed. After surmounting difficulties involving

FIGURE 9. Epitaxial thin films of Al (right) are grown on Si(111) substrates (left) under ultra-high vacuum conditions. Si(111) with epitaxial later chosen due to known growth conditions and similarity to other hydrogen-storage materials. (See, e.g., Hasan, *et al.* [3]).

substrate preparation and installation of the deposition apparatus, test runs were promising, leading to final preparation of epitaxial thin films of Al on Si(111) substrates, Figure 9, of which initial resistivity measurements for suitability were made last quarter. These Al films will be used to investigate the properties of undoped and Ti-doped Al surfaces in the presence of hydrogen in a controlled fashion, without mechanical alloying, to answer the fundamental question about the atomic-level mechanisms of hydrogen uptake and release from clean and poisoned surfaces. Future work may expand these initial efforts to other systems.

Conclusions and Future Directions

- Identified high-T phase of LiBH_4 via molecular dynamics modeling and matched with experiment data.
- Completed work on theory to address reliably the thermodynamics in molecular solids, using molecular dynamics modeling of LiBH_4 as case study (see publications).
- Completed joint theory effort on poisoning effects on Li-, Na-, and K-based borohydrides that showed that disassociation of H_2O to hydroxides ($-\text{OH}$) limited reversibility in LiBH_4 (see publications, with SNL, HRL, Pitt, Georgia Tech).
- Proposed possible Mg/Li alanate storage system reactions to avoid poisoning issues (with SNL, HRL, Pitt/Georgia Tech).
- Addressed, both experimentally and theoretically, the stability of observed intermediate phase in $\text{Ca}(\text{BH}_4)_2$ and $\text{Mg}(\text{BH}_4)_2$ systems (with SNL). Found stable $\text{Ca}(\text{B}_{12}\text{H}_{12})_2$ intermediate relative to those used to obtain initial $\text{Ca}(\text{BH}_4)_2$ (with SNL). A manuscript has been submitted for publication.
- Completed grain-size analysis of complex hydrides.
- We initiated study of MgH_2 and Mg nanoparticles and their interaction with carbon-based supports, such as aerogels. We find similar results to de Jonge *et al.* [4] for free clusters, showing extremely distorted particles even with 31 molecular units, in

distinction to studies by Larsson et al. [5] which did not permit global relaxations. We provided these to Mark Allendorf and collaborators in Berkeley to help seed one of their quantum Monte Carlo investigations for cluster/support investigations.

- The concentration of Ti needed to activate the AlH_3 -TEDA system is significantly less than that added, with losses of Ti of up 90% being found.

Future directions include:

- Continue surface science study for reaction of H_2 with clean and poisoned Al surfaces.
- Complete study of $\text{Ca}(\text{BH}_4)_2$ systems (with SNL), both experiment and theory.
- Continue work on evaluation of ball milling for mixing of catalysts.
- Continue investigation of hydrogen storage MOFs using tomography.
- Continue our investigation of the compositional difference in the Al_3 -TEDA system.

For Fiscal Year 2010 we will continue experimental studies of the microchemical and microstructural changes occurring in different candidate systems that are supplied by the various partners. In addition to electron diffraction and energy dispersive spectroscopy analysis, electron energy loss spectroscopy will continue to be a powerful tool to be applied to partner systems to identify electronic states within the materials. In addition, the recent addition of electron tomography to our suite of tools allows 3-dimensional information to be obtained from ball-milled materials. This allows the position, surface or embedded, of the catalyst particles to be determined. In addition, a new effort to analyze surface states that is ramping up this year will continue to provide useful results in FY 2010.

Electronic-structure methods will be used to support the surface-science experiments planned on Al (cleaned and poisoned). In addition, we will complete several studies involving stability of bulk $\text{Ca}(\text{BH}_4)_2$ and clusters of Mg and MgH_2 . We will complete studies of nanocluster structures of MgH_2 and NaAlH_4 *with and without* interactions to a carbon support (approximating interactions with aerogels). We are determining the effects of nanosize and support interactions on H desorption. Results of these studies may require experimental verification and we will collaborate with partners as appropriate. Additional calculations will be performed with input from partners regarding key issues.

We will continue to develop and enhance our electron tomography techniques as we apply it to

hydrogen storage MOF systems. Current limitations on data set size and reconstruction speeds have been overcome with the purchase of a new computer workstation designed for such processor- and memory-intensive applications.

FY 2009 Publications/Presentations

1. N.A. Zarkevich, and D.D. Johnson, "Predicting Enthalpies of Molecular Substances: exemplified *via* LiBH_4 ". *Physical Review Letters* 100, 040602-4 (2008).
2. N.A. Zarkevich, Teck L. Tan, L-L. Wang and D.D. Johnson, "Low-energy antiphase boundaries, degenerate superstructures, and phase stability in frustrated Ising model and Ag-Au alloys," *Phys. Rev. B* 77, 144208-9 (2008).
3. Bing Dai, Rees B. Rankin and J. Karl Johnson, Mark D. Allendorf, David S. Sholl, N.A. Zarkevich, and D.D. Johnson, "Influence of Surface Reactions on Complex Hydride Reversibility," *J. Phys. Chem. C*, 112 (46), 18270-18279 (2008).
4. L.-L. Wang, D.D. Graham, E. Ronnebro, I.M. Robertson, D.D. Johnson. "On the reversibility of $\text{Ca}(\text{BH}_4)_2$ hydrogen-storage reactions: microstructural and chemical characterization via experiment and theory," submitted.
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6. N.A. Zarkevich, S.V. Alapati, D. Sholl, and D.D. Johnson, "Prediction of enthalpies and van't Hoff plots of multiphase chemical reactions", in preparation.
7. D.D. Graham, J. Graetz, J. Reilly, I.M. Robertson. "Electron microscopy of AlH_3 : location of dopant in reversible Alane." In preparation.
8. D.D. Graham, I.M. Robertson. "Evaluation of ball milling for incorporation of in catalysts in Mg and Ca complex hydride-storage materials". In preparation.

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5. Larsson et al, *PNAS* (2007).

IV.A.1m Preparation and Reactions of Complex Hydrides for Hydrogen Storage: Metal Borohydrides and Aluminum Hydrides

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Project Start Date: April 1, 2005

Project End Date: September 30, 2010

Objectives

ORNL is conducting research to develop the chemistry for a reversible hydrogen storage system based on complex hydrides, chosen mostly from the borohydrides, amine borohydrides, amides/imides, alane or the alanates of the light elements in the periodic table that will achieve the DOE/FreedomCAR performance targets for 2010.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) System Weight and Volume
- (P) Lack of Understanding of Hydrogen Chemisorption and Physisorption

Technical Targets

ORNL is investigating high wt% materials, and efforts are directed toward making the release and uptake of hydrogen reversible. Percentages in Table 1 are for H₂ release only.

TABLE 1. Progress towards Meeting Technical Targets for Reversible Hydrogen Storage

Characteristic/ System	Units	2010/2015 DOE Targets/ Theoretical	ORNL observed
System Gravimetric Capacity	wt% (kg H₂/kg system x 100)	6%/9%	—
Al(BH ₄) ₃	—	16.92%	14.5%
Al(BH ₄) ₃ (NH ₃) ₂	—	17.19%	15.2%
Al(BH ₄) ₃ (NH ₃) ₃	—	17.26%	16.0%
Mg(BH ₄) ₂ (NH ₃) ₂	—	16.0%	14.6%

Accomplishments

Progress was made toward preparing new materials and understanding the mechanism of hydrogen release from metal borohydrides:

- Initiated a study of ammine metal borohydride (AMBH) complexes: synthesis, structure, and potential as hydrogen storage materials.
- Mg- and Ca-AMBH were prepared via a solvent-free synthesis route.
- The solvent free reaction of anhydrous ammonia with Al(BH₄)₃ gives the product Al(BH₄)₃(NH₃)₂; reaction of ammonia with aluminum borohydride in toluene and ether solvents gives different products.
- Investigated ionic liquids as a reaction medium for regenerating alane. The AlH₄⁻ anion appears to react with the imidazolium cation of the ionic liquid. Further work on ionic liquids will be discontinued.

Introduction

The focus of work at ORNL is the development of new materials, synthetic methods for materials, and studies of chemical reactions and processes that will lead to materials that will achieve the DOE/FreedomCAR performance targets for 2010. ORNL generally develops synthetic methods based on methodology that offers the most potential for scaling to kilogram and greater lot size. Synthetic methods are being developed and reactions are being studied for two types of target materials for hydrogen storage: complex anionic materials (Metal Hydride Center of Excellence [MHCoe] Project B) and amide/imide (M-N-H) systems (MHCoe Project C). For both types of materials ORNL is seeking (a) methods to scale up synthesis of

known materials or new materials identified by MHCoe partners (b) development of new materials. ORNL is also collaborating with scientists at Brookhaven National Laboratory in MHCoe Project D, the alane focus group, with an emphasis on using the methods of solution inorganic and organometallic chemistry in an effort to develop or improve processes to regenerate alane.

Approach

Our research involves materials from both known synthesis as well as those from newly designed synthetic procedures. The primary method used to follow the progress of reactions which release hydrogen is by temperature programmed pressure measurements where gaseous reaction products other than hydrogen are analyzed using a mass spectrometer or by infrared spectroscopy. Hydrogen desorption and uptake are investigated in a traditional Sieverts apparatus. Fourier transform infrared spectroscopy, X-ray diffraction (XRD), and elemental analysis by inductively coupled plasma-atomic emission spectroscopy as well as solution nuclear magnetic resonance (NMR) are available at ORNL to characterize solid reaction products, and Raman and solid NMR are available through collaboration with MHCoe partners. Structural determination using high resolution synchrotron-based XRD is available through internal collaboration at ORNL. Each material will initially be examined in a dehydrogenization study, both with and without catalysts. Those materials found to be suitable hydrogen storage material candidates will then be examined for regenerative (hydrogen absorption) capability. From these results, chemical (and-or procedural) adjustment to the most promising of the materials will be made in order to obtain the optimal in hydrogen de/absorption capacity.

Results

The majority of research at ORNL during the review period involved a study of AMBH, obtained from the reaction of ammonia with a metal borohydride. Although other researchers are investigating these materials as well, a unique feature in our study is our use of a solvent-free reaction system in which anhydrous ammonia is directly reacted with a metal borohydride. Our study has included the reaction of ammonia with Mg, Ca, and Al borohydrides, and for all three metals we can easily form the AMBH as a completely solvent-free product by direct reaction. This amination of the metal borohydrides was also shown to provide very important and desirable material properties as well as an increase in the amount of hydrogen desorbed in the case of Mg and Al borohydrides.

The Mg-AMBH is a quite promising material that was previously reported by Soloveichik, et al. [1]. Our innovation is the preparation of this compound by the direct (solvent free) reaction of anhydrous ammonia with magnesium borohydride. This material exhibits a remarkably low temperature for desorption compared to its parent metal borohydride, and our work shows it undergoes a fairly clean hydrogen desorption reaction, lacking any trace of by-products such as ammonia or diborane as observed by mass spectrometry. The quantity of hydrogen produced in the desorption indicates the ammonia is serving as a source of hydrogen as well as the borohydride. Interestingly, although $\text{Mg}(\text{BH}_4)_2$ was found to undergo a completely solid state desorption, the Mg-AMBH melts just prior to the H_2 desorption ($\sim 97^\circ\text{C}$). The solid magnesium:nitrogen:boron product following desorption of the hydrogen is amorphous to XRD and remains unidentified. To assist in the identification of the residue, we obtained ^{15}N -labeled ammonia and prepared a sample of $\text{Mg}(\text{BH}_4)_2(^{15}\text{NH}_3)_2$. This sample was given to our collaborators at the Jet Propulsion Laboratory and Caltech for analysis of the reaction product residue by high resolution ^{15}N -magic angle spinning-NMR (MAS-NMR). This experiment is still in progress.

The temperature programmed desorption of the Ca-AMBH yielded disappointing results. Although this material was easily synthesized (as either a mono or diamine species) via the solvent-free method, it was found that this material loses the NH_3 at a much lower temperature than that for hydrogen desorption. Several studies with a Sievert's apparatus proved that the material easily transformed back into $\text{Ca}(\text{BH}_4)_2$ prior to H_2 desorption, and then simply followed the usual desorption path previously shown for solvent free calcium borohydride. On a positive note, we found that even the solvated $\text{Ca}(\text{BH}_4)_2$ -tetrahydrofuran (THF) (as purchased from Aldrich) can be easily transformed into $\text{Ca}(\text{BH}_4)_2 \cdot 2\text{NH}_3$ and then subsequently converted to the solvent-free $\text{Ca}(\text{BH}_4)_2$ as the ammonia is released. This reaction could be potentially useful for preparing $\text{Ca}(\text{BH}_4)_2$ in the pores of a carbon scaffold. The $\text{Ca}(\text{BH}_4)_2$ could be deposited in the pores in THF solution, the THF removed by formation of the NH_3 adduct, and the NH_3 removed by thermal treatment. The ammonia adduct of LiBH_4 was also observed to evolve ammonia prior to loss of hydrogen from the borohydride [2].

Aluminum borohydride was found to readily react with anhydrous ammonia in a 1:2 ratio in the absence of solvent to form $\text{Al}(\text{BH}_4)_3 \cdot 2\text{NH}_3$. The formation of this Al-AMBH resulted in a greatly increased material stability relative to the parent metal borohydride. While the volatile $\text{Al}(\text{BH}_4)_3$ (a liquid at room temperature) is explosive in air, its ammine counterpart is a white solid that only slowly decomposes in air and gently bubbles hydrogen as water is added. This same increase of

material stability has been noted with the ammination of the magnesium and calcium borohydrides as well. The H_2 desorption study of this Al ammine metal borohydride demonstrate that the added ammonia is actually contributing to the wt% hydrogen desorbed from the material as was observed for the Mg-AMBH. The temperature programmed desorption data is shown in Figure 1. Mass spectrometry analysis of the gas desorbed from the Al-AMBH has revealed trace amounts of ammonia, diborane, and borazine, $B_3H_3N_3H_3$, suggesting that the desorption reaction involves reaction of BH_3 and NH_3 components, facilitated by the Al(III), to form ammonia borane or another BHNH species. The decrease in hydrogen evolution at 100 bar H_2 pressure offers some hope that the system can be at least partially regenerated.

Preparation of Al-AMBH was investigated by reaction of ammonia with aluminum borohydride in toluene and in ether, and the products were different than that formed in the solvent free reaction as shown by XRD and elemental analysis. In toluene, the composition is very close to that prepared under solvent free conditions, and the composition is $Al(BH_4)_3(NH_3)_3$. The reaction in diethyl ether is quite different and involved loss of one BH_3 group prior to precipitation of the Al-AMBH. The structures of the materials prepared in solution were determined using high resolution XRD data collected at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory. Although the $Al(BH_4)_3 \cdot 2NH_3$ material formed in the solvent free reaction has enhanced stability to air and water over the parent borohydride, we have discovered that the initially formed Al-AMBH slowly decomposes in the solid state into another phase (as detected by powder XRD). For this reason we were unable to determine the structure of this material during our experimental run at NSLS. The solvent-free Al-AMBH product was slowly transformed into two phases over time at room temperature with the

evolution of gas which included some diborane. One of the reaction products seems to be identical to the product formed in ether solution

The product formed in toluene has the structure shown in Figure 2 in which the Al centers have trigonal bipyramidal geometry with axial ammonia groups coordinated to the Al(III) sites. A view of the unit cell shows an additional ammonia group loosely associate with one of the borohydrides. We presume that the structure of the solvent-free product $Al(BH_4)_3(NH_3)_2$ has coordination about the Al site analogous to that shown in Figure 2. The temperature programmed desorption of $Al(BH_4)_3(NH_3)_3$ is shown in Figure 3. The total amount of hydrogen desorbed by this material at $550^\circ C$ is 16%, a value that rivals such chemical hydrides as NH_3BH_3 . Furthermore the mass spectrometry of the evolved gases from the stoichiometrically balanced $Al(BH_4)_3(NH_3)_3$ compound does not show evidence for even trace amounts of ammonia, diborane, or borazine. Formation of a borane ammonia adduct is likely occurring but the residue is amorphous, and vibrational spectroscopy and

FIGURE 2. Structure of $Al(BH_4)_3(NH_3)_3$ prepared in toluene solution determined from high resolution XRD indicating trigonal bipyramidal coordination of the Al site. Aluminum, red; boron, blue; nitrogen, green. The positions of hydrogen atoms were not resolved.

FIGURE 1. Temperature programmed desorption of hydrogen from $Al(BH_4)_3(NH_3)_2$ prepared by solvent free reaction under vacuum and under 100 Bar H_2 pressure.

FIGURE 3. Temperature programmed desorption of hydrogen from $Al(BH_4)_3(NH_3)_3$ prepared in toluene solution under vacuum.

solid state MAS-NMR will be utilized to identify the product.

Reaction of $\text{Al}(\text{BH}_4)_3$ with NH_3 in ether solution led to the evolution of gas including diborane and possibly some hydrogen. The structure of the product which precipitated from solution was determined from high resolution XRD data, and the structure confirms chemical analysis which indicated the Al:B ratio was 1:2. The structure shown in Figure 4 indicates discrete Al dimers having double amide bridges between two Al(III) centers, each with two terminal borohydride groups and one ammonia filling out the coordination sphere. The composition is best described as $[\text{Al}(\text{BH}_4)_2(\text{NH}_3)(\text{NH}_2)]_2$. This structure is quite informative because it offers insight into the potential decomposition mechanism of Al-AMBH compounds leading to hydrogen formation. It has been our contention that the first step in the decomposition of metal borohydride compounds is the formation of a metal hydride and borane. The decomposition of $\text{Al}(\text{BH}_4)_3(\text{NH}_3)_2$ leads to initial formation of an aluminum hydride which reacts with the coordinated ammonia of another molecule leading to hydrogen evolution and formation of a bridged amide group.

Further evidence for this pathway comes from isotopic labeling studies in which the initial hydrogen

FIGURE 4. Structure showing the unit cell of $[\text{Al}(\text{BH}_4)_2(\text{NH}_3)(\text{NH}_2)]_2$ prepared in ether solution as determined from high resolution XRD indicating bridged amide ligands between Al sites. Aluminum, red; boron, blue; nitrogen, light blue. The positions of hydrogen atoms were not resolved

evolved from $\text{Al}(\text{BH}_4)_3(\text{ND}_3)_2$ is predominantly mass 3 indicating it is deuterium hydride, where the H originates from BH_4^- and D from ND_3 . Future work will include an attempt to prepare and study the decomposition of $\text{Al}(\text{NH}_2\text{BH}_3)_3$ to understand whether ammonia borane is a possible intermediate.

The use of ionic liquids as a possible medium for the regeneration of alane was investigated since ionic liquids favor polar transition states. As a part of this work we attempted preparation of the ionic liquid 1,2-dimethyl-3-N-butylimidazolium tetrahydroaluminate. The AlH_4^- anion appears to react with the imidazolium cation of the ionic liquid. Further work on ionic liquids as a reaction medium will be discontinued.

Conclusions and Future Directions

Progress has been made in preparing ammonia metal borohydrides by a solvent free method, and progress has been made in understanding the mechanism by which hydrogen is evolved from metal borohydrides and ammonia metal borohydrides. The chemistry of aluminum borohydrides has proven to be quite rich, and preparation of $^{15}\text{NH}_3$ derivatives of Al-AMBHs will be productive for analysis of reaction products by ^{15}N MAS-NMR. We intend to continue study of aluminoboranes in collaboration with J.-C. Zhao, (Ohio State University).

- Determine the yield of the $\text{B}_{12}\text{H}_{12}^{2-}$ species in desorption of $\text{Mg}(\text{BH}_4)_2$ in borohydride eutectic melt, a continuation of work reported in Fiscal Year 2008. We want to prepare and study the decomposition of $\text{Mg}(\text{B}_3\text{H}_8)_2$ to understand how borohydride clusters form so that the hydrogenation process can be made reversible.
- Continue our study of the AMBHs, looking at how mixtures and catalysts might affect the desorption/absorption processes. As a part of that study we will develop a synthesis of titanium borohydride and titanium ammine borohydride and investigate stability and desorption characteristics of the latter.
- We will investigate the hydrogen desorption chemistry of alane amines ($\text{AlH}_3 \cdot n\text{NH}_3$) and the reactions of alane alkylamines AlH_3NR_3 as reducing agents.

FY 2009 Publications/Presentations

1. Ji-Cheng Zhao, Douglas A. Knight, Gilbert M. Brown, Chul Kim, Son-Jong Hwang, Joseph W. Reiter, Robert C. Bowman Jr., Jason A. Zan, and James G. Kulleck, "Study of Aluminoborane Compound $\text{AlB}_4\text{H}_{11}$ for Hydrogen Storage," *J. Phys. Chem. C*, **2009**, 113 (1), 2-11.
2. "Hydrogen Desorption/absorption Studies of Metal Boron Hydride Compounds" D.A. Knight, G.M. Brown, and J.H. Schneibel, oral presentation 236th National Meeting of the American Chemical Society in Philadelphia, PA August, 2008.

3. “Solvent-Free Synthesis and Hydrogen Sorption Properties of Ammine Metal Borohydrides,” G.M. Brown, D.A. Knight, J.H. Schneibel, C.J. Rawn, and J. Bai, oral presentation *237th National Meeting of the American Chemical Society* in Salt Lake City, UT March 22–26, 2009.
4. “Ammine metal borohydrides as hydrogen storage materials,” D Knight, G. Brown, Claudia Rawn, oral presentation *NHA Conference and Hydrogen Expo*, March 30–April 3, 2009, Columbia, SC.

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2. Simon R. Johnson, William I.F. David, David M. Royse, Marco Sommariva, Christina Y. Tang, Francesca P.A. Fabbiani, Martin O. Jones, Peter P. Edwards, “The Monoammoniate of Lithium Borohydride, $\text{Li}(\text{NH}_3)\text{BH}_4$: An Effective Ammonia Storage Compound,” *Chemistry - An Asian Journal*, 4, 2009, 849-854.

IV.A.1n Development and Evaluation of Advanced Hydride Systems for Reversible Hydrogen Storage

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Contract Number: DE-AI01-05EE11105

Subcontractor:
California Institute of Technology,
Solid-State NMR Facility, Pasadena, CA

Project Start Date: April, 2005
Project End Date: December, 2009

Objectives

- Develop and demonstrate light-metal hydride systems that meet or exceed the 2010/2015 DOE goals for on-board hydrogen storage.
- Validate initial storage properties and reversibility in light element hydrides by providing identification of phases and reaction pathways.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan (MYRDDP):

- (A) System Weight and Volume
- (D) Durability/Operability
- (E) Charging/Discharging Rates
- (P) Lack of Understanding of Hydrogen Physisorption and Chemisorption

Technical Targets

Regarding the technical barriers addressed by JPL's activities within the Metal Hydride Center of Excellence (MHCoE), the best representation of technical progress would probably be given by the maximum reversible

fraction of the material systems investigated, with the relevant 2010 target listed in the MYRDDP as 4.5% reversible H_2 content by weight in the engineered system. The material encapsulated in that system, obviously, must possess a higher content of H_2 , perhaps in the 9–12% range. For several reasons, the $Ca(BH_4)_2$ system (theoretical 12 wt%) appeared to be a practical reality at the early part of the year, but with less than 6% reversible capacity on first absorb/desorb cycle – and less so after that – this material was shown to have serious issues. Still, as the only practically reversible borohydride in the MHCoE arsenal, much attention was given to its associated reaction paths.

Accomplishments

- Provided phase characterization, kinetics (i.e., diffusion behavior), and reversibility assessments via magic angle spinning nuclear magnetic resonance (MAS-NMR) in numerous systems (i.e., Li-Mg-B-H, Li-Sc-B-H, Li-B-Ca-Al-H, AlH_3 , Li-Mg-Al-N-H).
- Determined the $MB_{12}H_{12}$ systems ($M = Li, Mg, Ca$) have unique affinities for water of hydration, presenting potential difficulty for manufacturing and distribution of these materials.
- Demonstrated the lack of destabilization in the $Li_2B_{12}H_{12} + MH_2$ ($M = Mg, Ca$) system, in disagreement with theoretical predictions.
- Demonstrated the unique nature of NMR analysis in identifying the character of B-H bonding and reaction pathways in the metal-borohydride systems; this technique can distinguish amorphous/nanophase species that are not otherwise sensible via X-ray diffraction (XRD) or vibrational spectroscopy methods.
- As part of an Ohio State University (OSU)/Oak Ridge National Laboratory (ORNL)/Caltech/JPL team, discovered a new storage material, AlB_4H_{11} , giving initial capacity of 11% H_2 by weight.

Introduction

Activities at JPL under the auspices of DOE's MHCoE are designed to contribute to the development of light-metal hydride systems that meet or exceed the DOE/FreedomCAR technical targets for on-board reversible hydrogen storage. JPL performs in several different roles in the Center. The major portion of the effort at JPL is dedicated to validating initial storage

properties (2010 target: >4.5 wt% reversible gravimetric, 28 g/l volumetric hydrogen capacity) of novel light element metal hydrides including destabilized hydride systems containing LiH, MgH_2 , and LiBH_4 , complex amide/imides, borohydrides, and AlH_3 -based hydrides as well as other promising samples provided by many MHCoe partners; significant attention has been paid to the $\text{B}_{12}\text{H}_{12}^{2-}$ system and associated reaction pathways. In addition, JPL has a role within MHCoe to assess the reversibility and durability of the more promising hydrides during cycling.

In the course of these tasks, various solid state NMR studies and other analytical techniques were used to assess promising “catalyzed” complex hydrides including alanates and borohydrides for their kinetics and reversibility to improve their practical hydrogen storage potentials. Such techniques have proven quite powerful for characterization of hydrogen and metal diffusion behaviors as well as critical phase transformation processes.

Approach

JPL's participation in the MHCoe continues as a widespread effort, involving all the individual projects within the Center scope. In the area of complex anionic materials, JPL continues to work closely with Sandia National Laboratories (SNL) towards an understanding of the characteristics of the $\text{Ca}(\text{BH}_4)_2$ system; borohydrides from OSU, ORNL, Caltech, General Electric, University of Hawaii (UH), and Savannah River National Laboratory have also been part of JPL's collaborative role. JPL has also actively participated in the discovery and characterization of destabilized Mg/Li/N systems in collaboration with Center partners UH, University of Utah (UU), the National Institute of Standards and Technology (NIST) and SNL.

A comprehensive materials development and characterization program continues to be the central focus of JPL's many roles in MHCoe. Of primary importance is the use of volumetric measurements to determine hydrogen storage capacities and equilibrium pressures on destabilized nanophase and complex metal hydrides. In addition, powder XRD may be used at JPL to determine material compositions where applicable. In collaboration with the Solid-State NMR Facility at Caltech, MAS-NMR measurement techniques can be applied; these measurements are crucial for gaining an understanding of phase compositions and bonding characteristics in these material systems. Caltech also provides the capability for Raman spectroscopy measurements for the elucidation of additional material characteristics; some of these, such as hydration state and bond parameters, are subtle and can provide good correlation with other techniques applied by the JPL-Caltech team.

Results

Project A

JPL's efforts within MHCoe Project A (Destabilized Hydrides) focused on the investigation of the possibility that the $\text{Li}_2\text{B}_{12}\text{H}_{12}$ system could be destabilized with the introduction of simple binary metal hydrides. The expectation of destabilization was provided by a theoretical development of these material systems, showing various reaction pathways in which the effect was predicted. In the resulting experiments at JPL and Caltech, $\text{Li}_2\text{B}_{12}\text{H}_{12} + \text{MH}_2$ ($\text{M}=\text{Mg}, \text{Ca}$) which were reported to have favorable ΔH_{react} , appear to show a high kinetic barrier (Table 1).

TABLE 1. $\text{Li}_2\text{B}_{12}\text{H}_{12} + \text{MH}_2$ Systems Investigated for Destabilization Effects

Reaction	Description
$\text{Li}_2\text{B}_{12}\text{H}_{12}$	Desorbed 450°C,
$\text{Li}_2\text{B}_{12}\text{H}_{12}$	Reabsorbed 450°C, 90 atm H_2
$\text{Li}_2\text{B}_{12}\text{H}_{12} + 6\text{MgH}_2$	Desorbed 400°C
$\text{Li}_2\text{B}_{12}\text{H}_{12} + 6\text{MgH}_2$	Reabsorbed 300°C
$\text{Li}_2\text{B}_{12}\text{H}_{12} + 2\text{CaH}_2$	Desorbed 400°C

In addition, Figure 1 shows that ^{11}B MAS-NMR results show little change in B-H coordination from initial dodecaborane structures following the reaction attempts.

Project B

Within MHCoe Project B (Complex Anionic Materials), JPL performed a great deal of work relating

FIGURE 1. ^{11}B MAS NMR spectra showing the lack of predicted destabilization effects in the $\text{Li}_2\text{B}_{12}\text{H}_{12} + \text{MH}_2$ ($\text{M} = \text{Mg}, \text{Ca}$) system.

to phase identification and reaction elucidation of the various borohydrides. In the $\text{Ca}(\text{BH}_4)_2$ system, partial reversibility of the compound at reasonable conditions (330°C , 80 bar) was seen via MAS-NMR. In Figure 2, MAS-NMR shows the confirmation of the system's reversibility. Following hydrogenation at 330°C , about 57% of boron is now present as $\alpha\text{-Ca}(\text{BH}_4)_2$; the intermediate $\sim 30\%$, $\text{CaB}_6 \sim 13\%$. In other samples provided by SNL, the use of catalyst showed change of crystalline polymorphs of the rehydrogenated powder ($\alpha \rightarrow \beta$ phase). This interesting result shows various additional transformations among different polymorphs around the reaction temperature. Figure 3 shows that although the Ca-B-H intermediate is not yet fully characterized, its chemical shift is very close to $\text{CaB}_{12}\text{H}_{12}$.

Various dodecaborane samples were characterized by NMR and other spectroscopic tools in collaboration with SNL, S. Jalisatgi (University of Missouri-Columbia), J.-C. Zhao (OSU), and T. Udovic (NIST). Figure 4 shows NMR spectra from the results of this study. In addition, ^{11}B MAS-NMR spectra show that the BH_4 icosahedrons become highly mobile as water molecules are introduced to the crystalline phases. The most significant finding in this regard is the suggestion that removal of crystalline water may become a challenging issue for certain metal cations (e.g. Mg) in the polyborane system; this special water affinity may present issues for the manufacture and maintenance of borohydride storage systems in the practical aspect.

In a related study, direct dehydrogenation of $\text{Li}_2\text{B}_{12}\text{H}_{12}$ material was attempted in order to elucidate reaction pathways in the M-B-H system ($\text{M} = \text{Li}, \text{Mg}, \text{Ca}$). While probably not a practical storage medium,

the lithium dodecaborane salt presents a reasonable experimental system in which to study the mobility and reactivity of the BH_4/BH_3 anion. Dehydrogenation to 500°C of 525 mg of this material yields an initial 3.7% loss, with most activity occurring between $300\text{--}400^\circ\text{C}$. Based on several experiments, it appears that in the $\text{MB}_{12}\text{H}_{12}$ system ($\text{M} = \text{Li}, \text{Mg}, \text{Ca}$), high affinity with H_2O results in B-OH formation during heating, even as water

FIGURE 3. ^{11}B MAS NMR spectra of several samples of $\text{Ca}(\text{BH}_4)_2$ in different stages of hydrogenation/dehydrogenation. The dotted line indicates the presence of an intermediate compound in the dehydrogenation product that despite its shift alignment with the reference $\text{CaB}_{12}\text{H}_{12}$ may be unique and unidentified. Dissolution of the desorbed material in water did not show the presence of the $[\text{B}_{12}\text{H}_{12}]^{2-}$ phase, unlike LiBH_4 or MgBH_4 cases.

FIGURE 2. ^{11}B MAS NMR spectra following the rehydrogenation of $\text{Ca}(\text{BH}_4)_2$ at 330°C . The crystalline phase $\text{Ca}(\text{BH}_4)_2$ is seen after absorption via the powder pattern from the spinning sidebands and chemical shift position of the subject peaks.

FIGURE 4. ^{11}B MAS NMR spectra showing the results of a study of metal-dodecaborane materials. One can see characteristic down field shifts for polyborane compounds with alkali metal vs. alkali earth metal cations.

is being removed. The conclusion reached at this stage is that the presence of water in these material systems proves a universal difficulty in practice as there are several hydration states in each system.

In addition, JPL and Caltech collaborated with OSU and ORNL in the discovery of a new type of aluminoborane material that looks promising for storage. The $\text{AlB}_4\text{H}_{11}$ compound was developed jointly by OSU/ORNL, with JPL/Caltech providing volumetric/kinetic measurements and NMR spectroscopy. Extensive characterization of this new material, produced by ORNL, gave a capacity of 11.4% H_2 by weight via 400°C desorption (see Figure 5); most significantly, however, a large portion of the H_2 release occurred in the range 140-200°C. Initial NMR spectra revealed a complex boron environment in the products, including both B-H complexes and possibly elemental boron with other features, partially avoiding the $\text{B}_{12}\text{H}_{12}$ route.

Project C

In MHCoE Project C (Amides/Imides), JPL played a role in the investigation of the $\text{Li}_3\text{AlH}_6 + \text{Li}_2\text{NH}$ system via NMR, in collaboration with Z. Fang at UU, who provided samples for NMR spectroscopy.

It was determined that preferential formation of AlN or Li_3AlH_6 depends on heating rate; Li_3AlH_6 formation needs heating rate of 5°C/min, and $T_{\text{react}} > 250^\circ\text{C}$. Characterization of this system has shown the collaborators that MAS-NMR can be a good probe of pathways via ^{27}Al spectra.

Conclusions and Future Directions

As currently planned, the MHCoE project will be coming to an end in December 2009. Nevertheless, there are several broad areas in which JPL plans specific accomplishments, mostly based upon progress made over the course of the project. These areas, then, are the means by which JPL hopes to “sum up” its materials development and characterization efforts.

- **Project A - Destabilized Hydride Systems**
 - Fiscal Year 2009: Investigate the potential for structured carbon-based materials (aerogels, graphitic carbons, high-surface area materials) as dopants in destabilized hydride systems utilizing volumetric, NMR, and XRD techniques.
 - Investigate pore size effects.

FIGURE 5. Experimental volumetric results from the desorption of $\text{AlB}_4\text{H}_{11}$, showing a mobile H_2 content in excess of 11% by weight. ^1H NMR suggests partial reversibility of an H_2 bearing phase, and ^{27}Al NMR following reabsorption suggests the possibility of reduced Al metal, but this is a topic for further study.

- **Project B - Complex Anionic Materials**

- FY 2009: Continue phase transformation and reversibility studies of the $\text{Ca}(\text{BH}_4)_2$ system in collaboration with MHCoE partners, lending support with volumetric characterizations as well as MAS-NMR, XRD, and Raman analytical techniques.
- FY 2009-2010: Assess initial cycling data for $n \sim 10$ -100 cycles (SNL, Caltech, UH). Continue studies of possible destabilization routes in material systems containing the $[\text{B}^{12}\text{H}^{12}]^{2-}$ anion, especially as it pertains to avoiding the production of this stable intermediate in the Mg-B-H, Li-B-H, Ca-B-H and mixed cation borohydride systems.

- **Project C - Amides/Imides**

- FY 2009-2010: Perform systematic investigations of ^{15}N -enriched amine-borohydride materials, leveraging MAS-NMR techniques for the purpose of assessing reaction kinetics, bonding dynamics, and phase transformation effects in the M-B-N-H system ($M = \text{Li, Al, Mg}$), especially for mixed cation and/or ternary systems.

FY 2009 Publications/Presentations

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IV.A.1o Effect of Gaseous Impurities on Durability of Complex Li-based Hydrides for Hydrogen Storage

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Objectives

- Determination of the effect of ppm level impurities in H₂ gas as well as the effect of impurities and defects in light-weight storage materials.
- Evaluate the long-term durability of light weight Li-N-based compounds.
- Understand the reaction pathways for both developing new materials with enhanced hydriding

properties, modifying or controlling reaction pathways for improved performance.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) System Weight and Volume
- (D) Durability/Operability
- (E) Charging/Discharging Rates
- (K) System Life Cycle Assessments
- (P) Lack of Understanding of Hydrogen Physisorption and Chemisorption

Technical Targets

This project is conducting fundamental studies of light weight hydrogen storage materials, particularly of the Li-N-H system. Insights gained from these studies will be applied toward the design and synthesis of hydrogen storage materials that meet the following DOE 2010 hydrogen storage targets:

- System Gravimetric Capacity: 1.5 kWh/kg
- Storage System Cost: \$4/kWh net
- Cycle Life (1/4 tank to full): 1,000 cycles

Accomplishments

- Made progress in cycling tests on Li-N-H system to determine the effect of various gaseous impurities in H₂ (100 ppm levels of O₂, CO, H₂O, CH₄, NH₃) to simulate the charge/discharge with fresh H₂ in Li-N-H hydrides.
- The effect of NH₃ gas impurity-isothermal (255°C) and isobaric aging at 6.2 bar H₂ performed using 100 ppm NH₃ in H₂ revealed no significant loss in hydrogen capacity.
- Critical phase reaction pathways determined using progressive incremental loading of hydrogen in Li₃N, supported by calculation of phase diagrams (CALPHAD)-developed Li-N-H phase diagrams.
- Determined formation of the Li₄NH phase at room temperature; this phase is stable up to 5 wt% H and is a peritectically decomposed phase observed at 25°C.
- Details of the amount of LiH phase formed under equilibrium loading of hydrogen determined.

- New higher capacity solid-solution cubic phase of $\text{Li}_{2-x}\text{NH}_{1+x}$ type was found.
- Improved kinetics observed at higher pressures in the Li-N-H system.

Introduction

Light weight complex metal hydrides are becoming increasingly important for hydrogen storage due to its gravimetric and volumetric capacities. Gaseous impurities (ppm levels) in ultra-high purity (UHP) hydrogen may cause loss in hydrogen capacity during cycling. Extrinsic pressure cycling and thermal aging with impure hydrogen was used to evaluate capacity changes in this project; many of the tasks are complete. These tests are important for long-term reliability of metal hydrides that is important for working towards achieving DOE technical targets for a hydrogen economy. In general, UHP hydrogen is used in the research laboratory for the development of metal hydrides. However, commercial hydrogen will always have some very low level impurities (ppm levels); typically O_2 , H_2O , CH_4 , N_2 , hydrocarbons, and others in hydrogen. Typical industrial grade hydrogen, that we used showed: “Hydrogen min % (v/v) 99%, water ~32 ppm, O_2 ~10ppm, N_2 ~400 ppm, total hydrocarbons: 10 ppm, CO_2 ~10 ppm, CO ~10 ppm, argon may be present, reads as oxygen.” We also used special 100 ppm O_2 mixed with UHP hydrogen in this study. These low level impurities affect the performance of hydrogen storage materials in the hydride beds that are installed in automobiles. The purpose of the pressure cycling experiments (with fresh charges of impure hydrogen) is to simulate the long-term performance of metal hydrides with trace amounts of impurities in the hydrogen with the above mentioned gases. In addition, it is possible that by products of the hydrogen storage (side-reactions), such as, possible generation ammonia gas may occur and affect the storage properties. The degradation of the hydriding properties are generally associated with disproportionation or decomposition of hydrides surface or bulk properties of the material during normal periodic charges of impure hydrogen. These studies are expected to lead to the understanding of mechanisms that occur after “hydrogen filling” in tanks numerous times. In another situation, for example, a hydride bed is left unused for a prolonged period of time, i.e., hydrogen is fully loaded in a hydride bed from a gas station, this type of test is called *Thermal Aging*; performed at elevated pressures and temperatures.

The objective of this research is to investigate the effect of trace impurities in complex hydrides by the principal investigator’s (PI’s) group as well as Center partners which can be potentially used for fuel cell

and other applications and aid in the development of materials solutions to potential hydrogen sorption degradation problems. The relevance to the Metal Hydride Center of Excellence program is that, trace impurities in hydrogen gas will have an impact on the hydrogen loading capacities during periodic recharging with fresh hydrogen in practical applications. These tests are being performed by accelerated laboratory testing which are extremely useful to understand the reliable use of hydrogen fuel. The PI was on sabbatical leave at the University of Geneva, University of Paris, and Università di Roma “La Sapienza” where some of the work was performed.

Approach

In this research, we are conducting experiments on cycling and aging tests of materials (as described in the above section) developed by the Center partners. Pressure cycling apparatus was constructed at UNR for hydrogen loading and unloading. The overall approach to perform cycling on currently reversible complex hydrides such as imide/amide system (using Li_3N as precursor), Li amide-alanate that has theoretical hydrogen capacity ranging from ~7 to ~10.5 wt% hydrogen. The specific tasks were to determine the changes in the pressure-composition isotherm after cycling with impure hydrogen. A reference temperature of 255°C and a hydrogen pressure range from vacuum to 2 bar was chosen, based on pioneering research of Prof. Ping Chen’s *Science* paper [1].

We have expounded on the initial results obtained last year by performing crystal structure analyses after cycling steps, by obtaining isotherms with UHP hydrogen (after cycling with impure hydrogen). Crystal structure analyses were performed as well that revealed new phase formation, yet showed hydrogen storage properties. Characterization of the phases before and after these cycling tests was performed using both static and dynamic X-ray diffraction revealed the impurity related and intrinsic impurity phases after cycling. We performed synchrotron in situ X-ray diffraction on $\text{Ca}(\text{BH}_4)_2$ in collaboration with ESRF, France, and Sandia National Laboratories. In addition, studies were performed on the sabbatical leave in Geneva, Paris and Rome, where thermodynamic phase equilibria and crystallographic studies were performed.

Results

High resolution pressure-composition isotherms were obtained on the $\text{Li}_3\text{N-H}_2$ system (Figure 1) at the University of Genève. It can be noted there the isotherm exhibits a slope or a curvature at higher hydrogen compositions indicating a possible new plateau. However, this curvature was found to be due to the use of H/M rather than H/H+M. In Figure 1 there are two

isotherms superimposed, which show no significant change at lower hydrogen content, but at higher concentrations there is no absorption of hydrogen. It should be noted that in the case of heavy classical metal hydrides these difference in the calculation methods do not result in changes of the isotherm profile. Also, we have new high resolution very low pressure isotherms from UNR, obtained recently which gives more details.

In situ differential scanning calorimetry performed on the Li-N-H system showed that there were two possible melts during heating with hydrogen gas. Starting with Li_3N in hydrogen atmosphere we obtained data that suggests two possible melts around $\sim 50^\circ$ and $\sim 325^\circ\text{C}$ (endotherms) during heating. In the same experiment a cooling curve was also obtained. There is a large exothermic region (between 180° and 330°C) which does not correspond to Li_2NH to LiNH_2 transformation. More detailed studies are in progress in Reno, using industrial hydrogen gas environment in the differential scanning calorimeter.

Although detailed analyses are in progress, we show a section of the X-diffraction pattern that relates to the presence of Li_4NH and a new solid solution cubic phase in addition to Li_2NH (cubic phase). We determined details of phase transformations during hydriding of Li_3N by intentional termination of the hydrogenation at pre-determined compositions in a Sievert's apparatus. Crystal structure evaluation was performed by using X-ray diffractometry at room temperature on a series of samples. X-ray diffraction data (inset) shows details of phase transformations (Figure 2). We discuss only the formation of $\text{Li}_{2-x}\text{NH}_{1+x}$ phase here. Between 0.52 and 3.2 wt% H we found presence of Li_2NH phase. At higher H-concentration we found the Bragg peaks of a new solid solution phase $\text{Li}_{2-x}\text{NH}_{1+x}$ up to 8.1 wt%. At 9.5 wt% H, we found Bragg peaks corresponding to LiNH_2 . We also found the compositions at which

Li_4NH is stable; up to 3.2 wt% H. The LiH phase begins to form at slightly higher pressures when hydrogen contents reach ~ 4.8 wt% H.

In another study, we confirmed the formation of hydride phases using quantitative X-ray diffraction analyses on two partially hydrogenated samples at ~ 1 and ~ 8 wt% H. At 1 wt% H we found 19 wt% Li_4NH phase, with 33 wt% Li_3N and other phases (Table 1). At 8 wt% there is a large amount of LiH (42.5 wt%). It is interesting to note that there small amount of LiNH_2 (8.5 wt% H) although this phase should form at ~ 8.78 wt% H; this is possibly due to a start of two phase region in the binary Li_3N - H_2 phase diagram.

TABLE 1. Quantitative Analysis of Phases Present after Loading of Li_3N to 1 and 8 wt%

Phase	wt% @ 1 wt% overall H ₂	wt% @ 8 wt% overall H ₂
LiNH_2	0	8.5
Li_2NH	43	41.5
Li_3N	33	2.5
Li_2O	2.5	5
LiH	2.5	42.5
Li_4NH	19	0

In an effort to characterize the *defect structure of the complex hydride precursors*, we added impurities to Li_3N . A very brief background is given below of the methodology. In this method we measure elastic energy dissipation coefficient that is given by $Q^{-1} = M''/M'$, where Q^{-1} is the elastic energy coefficient. A pulse is applied to the sample momentarily, and then turned off, and we measure the logarithmic decrement of the vibration

FIGURE 1. A baseline high resolution isotherm for the Li-N-H system, with Li_3N as starting material is shown obtained at University of Geneva. The inset shows very low pressure isotherm obtained at University of Nevada, Reno at 255°C .

FIGURE 2. X-ray diffraction pattern from several experiments showing evolution of the $\text{Li}_{2-x}\text{NH}_{1+x}$ phase above ~ 5 wt% H for hydrogen loading at 255°C . However, the patterns were taken at room temperature.

amplitude, through the width of the resonance curve as shown in the equations:

$$Q^{-1} = \frac{1}{\pi} \ln \left(\frac{A(t)}{A(t+T)} \right) \quad \text{and} \quad A = \frac{\text{const.}}{(\omega^2 - \omega_0^2)^2 + (\omega_0^2 Q^{-1})}$$

$$\text{where, } \omega = 2\pi f$$

$$M' = 0.95 \times \rho \times \left(\frac{l^2}{t} \right) \times f_0^2 \quad \text{where, } \rho \text{ is the density.}$$

Details can be found in the papers of O. Palumbo et al. [2] listed in this report. These studies in progress at Università di Roma “La Sapienza” (International Energy Agency [IEA] collaboration with Dr. Rosario Cantelli and co-workers); data will be reported later.

A detailed room temperature X-ray diffraction study of phase evolution was conducted in which the hydrogen loading experiments were performed at 255°C, and the samples were cooled to room temperature (at University of Geneva under IEA collaboration). The X-ray diffraction data was taken from samples at 0.52, 1.0, 1.7, 3.2, 4.9, 6.5, 8.1, and 9.5 wt% H. Care was taken to ensure that the pressure in the system did not rise above ~1 to 1.2 bar at each loading. First we will discuss the stability of the Li₄NH phase as a function of hydrogen concentration. It can be noted in Figure 3 that the Li₄NH concentration increases up to ~1.7 wt% then begins decreasing and finally and disappears at slightly >~4.9 wt%. The presence of this phase was first reported by Weidner et al. [3] by performing low pressure studies on amide-imide studies. We confirmed that this Li₄NH phase forms peritectically at lower temperatures up to about ~5 wt% H. Marx [4] synthesized single crystals of this phase at low temperatures and determined the structure. Also, once the Li₄NH concentration decreases, the Li₂NH concentration rapidly increases. Next we discuss the termination of Li₂NH at ~5 wt% H and start of Li_{2-x}NH_{1+x} phase (see Figure 3); the X-ray data for Figure 3 is shown in Figure 2. The LiNH₂ phase evolves around 8 wt% H. The concentration of LiH phase continues to increase up to ~8 wt% H. A small amount of Li₂O phase is present at all concentrations.

In the imide-amide system there is always concern that NH₃ emission may occur during loading/unloading of hydrogen, that may have an impact on stability of these hydride phase. Therefore, experiments were performed on the Li₃N-H₂ system by thermal aging with 100 ppm NH₃ in H₂ at 255°C at 6.3 bar. Isotherms were taken before and after aging for 3 and 23 days, as shown in Figure 4(a). It can be concluded that 100 ppm levels of NH₃ in H₂ are not detrimental to this Li-N-H system at 225°C. X-ray diffraction patterns taken with and without NH₃ aging are shown in Figure 4(b). X-ray diffraction patterns (blue) obtained from the hydrides obtained *before aging at low pressure* (<<1.3 bar)

FIGURE 3. The amount of phase evolved (y-axis) after various amount of hydrogen loading (x-axis). Note the growth and decrease of Li₄NH and LiH phases.

showed predominantly Li₂NH phase, and some impurity phase Li₂O, as expected. After aging with 100 ppm NH₃ @ 6.3 bar, the X-ray diffraction pattern (red) showed mainly LiNH₂, LiH, and small amount of Li₂O phase. These are also expected phases under the pressure conditions.

Thermodynamic CALPHAD modeling is in progress. We have developed Li-N-H ternary phase diagrams at (1) 255°C and 9 atm (under H₂ loading condition), (2) 25°C and 9 atm, and (3) 25°C and vacuum (unloading condition). The ternary Li-N-H phase diagrams, not shown here, indicate the reaction pathways for the composition of ~2.5 wt% H:

- (1) Li₂NH(s) + Li₃N + Li (liq.) – (small amount @ 225°C, 9 atm.)
- (2) Li₃N(s) + Li₂NH(s) + LiH(s) – (cooled to 25°C, 9 atm.)
- (3) Li₂NH(s) + Li₄NH + LiH (s) – (25°C, with all gaseous H₂ removed)

Conclusions and Future Directions

- In support of the DOE MHCoe mission, some critical aspects related to long term stability of light weight complex hydrides for vehicular applications are addressed. Durability/operability of complex hydrides was evaluated to understand the role of ppm gaseous impurities in hydrogen gas experienced

FIGURE 4. (a) Isotherms obtained before and after ammonia aging at 255°C at 6.3 bar with 100 NH₃/H₂ for 3 and 23 days, showing very little loss of capacity after 23 days. (b) X-ray diffraction pattern of sample taken before and after loading hydrogen with expected phases formed. At higher pressures, LiNH₂ phase is stable; but it is not a result of ammonia aging, just the experimental conditions.

during periodic filling at a commercial hydrogen gas station for future H₂ vehicles. Much of the data has been reported in previous years.

- Li-N-based compounds are used to evaluate long-term durability, reaction pathways for both developing new materials with enhanced hydriding properties as well as modifying or controlling reaction pathways for improved performance.
- Reaction pathways to overcome barriers that exist to improve the kinetics, lower hydrogen release temperatures, and extend cycle life are being determined. An example of stepwise incremental hydrogen loading is shown for Li₃N-H that exhibit three primary phase boundaries.
- Determined formation of the Li₄NH phase at room temperature; this phase is stable up to ~5 wt% H.
- Isobaric and isothermal aging at 255°C revealed that 100 ppm levels of NH₃ impurity exhibited virtually no loss of hydrogen capacity, whereas CH₄ impurities have low impact.

- A new non-stoichiometric Li_{2-x}NH_{x+1} cubic phase was found.

As for the future directions, we are continuing studies of cycling/aging with 100 ppm level impurities. We are developing thermal cycling experiment in which hydride samples will be cooled rapidly from 255°C to room temperature and reheated with hydrogen (rather than pressure cycling). In situ X-ray diffraction work will be used on newly developed hydride samples to understand reaction pathways with the goal of developing improved hydrides for vehicular applications.

FY 2009 Publications/Presentations

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2. W. Chien, D. Chandra, J.H. Lamb, "X-ray Diffraction Studies of Li-Based Complex Hydrides after Pressure Cycling," *Advances in X-ray Analysis*, vol. 51. p 190-195 (2008).
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4. O. Palumbo, A. Paolone, P. Rispoli, A. D'Orazio, R. Cantelli, and D. Chandra, "Decomposition reaction of lithium amide studied by anelastic spectroscopy and thermogravimetry" *International Journal of Materials Research, Zeitschrift fur Metallkunde*, Vol.9, 2008, 487-490. (not reported earlier).
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IV.A.1p Li-Mg-N Hydrogen Storage Materials

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Project Start Date: October 1, 2007
Project End Date: September 30, 2012

Objectives

- Determine the sorption kinetics for the transition metal catalyzed $\text{LiH/Mg}(\text{NH}_2)_2$ system.
- Verify reversibility conditions of TiCl_3 doped LiMgN .
- Explore the effect of catalyst loading on both charge and discharge reaction pathways and kinetics.
- Identify reversible hydrogen storage compounds in the mixed metal/mix amide-borohydride system.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan in descending order of impact:

- (A) System Weight and Volume
- (B) Charging/Discharging Rates

Technical Targets

This project includes both fundamental studies of the sorption kinetics in the mixed metal amide, $\text{LiH/Mg}(\text{NH}_2)_2$ system, as well as new materials discovery in the mixed amide/borohydride system. Insights gained from these studies will be applied toward the design of storage systems that meet the following DOE 2010 and 2015 hydrogen storage targets:

- System Gravimetric Capacity and Volumetric Density
- Charging/Discharging Rates
- Fuel Purity

- System fill time
- Minimum hydrogen delivery rate

Accomplishments

- Desorption products in all cases considered appear to be the same (mixture of LiCl , Mg_3N_2 , LiMgN and a minor amount of an unidentified phase [$<5\%$]).
- Ti is a catalyst for desorption but has minimal effect in absorption.
- Increased catalyst loading significantly affects H_2 discharge rate.
- Different kinetic modeling approaches are being applied to characterize and understand reaction mechanisms and to enable prediction of charge/discharge rates under varying conditions.
- A characteristic charging time (τ_{80}) of 30 minutes, calculated for the isothermal charging results, is faster than those presented for this material elsewhere in the literature.
- Reversible gravimetric storage density for the isothermal measurements is lower than that reported by Lu et al. [1] for the same material (~ 6.66 wt% versus ~ 8.0 wt%).
- The amorphous phase $\text{Li}_x\text{Ca}(\text{BH}_4)_x(\text{NH}_2)_y$ resulted in a dehydriding temperature 100°C lower than $\text{Ca}(\text{BH}_4)_2$.

Introduction

In an effort to identify and synthesize a reversible metal hydride material capable of meeting the 2010 and 2015 DOE FreedomCar technical targets, researchers are investigating various metal hydrides/catalyst combinations. To date, the most promising in situ reversible compound stemming from the Metal Hydride Center of Excellence (MHCoE) is $\text{LiH/Mg}(\text{NH}_2)_2$ [1,2]. This compound resides among a series of similar compound stoichiometries ranging from Li:Mg ratios of 1:1 through 4:1 [1-7]. It has been found that the greatest hydrogen absorbing material is LiMgN , which was reported to be reversible under fairly moderate conditions (160°C – 220°C for dehydriding, 160°C and 2,000 psi for rehydriding) [1]. Furthermore, the material has been reported to have a hydrogen storage capacity of (8.0–8.1) wt% [1], where the starting materials are LiNH_2 and MgH_2 combined in a (1:1) molar ratio with a small amount of TiCl_3 dopant. This study of the LiMgN used an autoclave-type high pressure charging apparatus and transient thermodynamic gravimetric analysis (TGA) measurements to confirm hydrogen storage capacities.

The work reported here was designed to compliment the work of Lu et al. [1], by thoroughly measuring the isothermal kinetic hydrogen charge and discharge rates and further optimizing the kinetics through compositional adjustments.

Approach

LiH/Mg(NH₂)₂

The previously identified LiMgN material was studied by ball milling the precursor LiNH₂ and MgH₂ materials with the TiCl₃ catalyst to ensure a well-mixed and controlled initial state in terms of particle size. Material for this study was Frisch milled with a ball mass to material mass ratio of 35:1, following the work of Lu [1]. A Sievert's apparatus was used to measure the isothermal kinetic rates of hydrogen charge and discharge. The present studies are intended to provide a detailed understanding of the isothermal kinetics of charging and discharging of the material, in addition to tabulations of the weight percent of hydrogen stored under specified conditions. The parameters that are explored in the current study are charge and discharge temperature, charge and discharge pressure, and the catalyst loading used to activate the material.

Mixed Amide/Borohydrides

The synthesis of materials was accomplished by ball milling one component metal borohydride (e.g. Ca(BH₄)₂) with another metal amide (e.g. LiNH₂). These precursors are available commercially through Aldrich, with others such as Mg(BH₄)₂, Mg(NH₂)₂ and Ca(NH₂)₂ prepared by established procedures [4-6, respectively]. Once the components metal hydrides are ball milled, powder X-ray diffraction (XRD) was used as the initial screening tool. Fourier transform infrared spectroscopy (FTIR), Raman and nuclear magnetic resonance will also be used to verify the formation of new compounds. Where ball milling does not yield suitable materials, wet chemical synthesis techniques will also be employed in which the metal hydrides are mixed within a suitable solvent under inert atmosphere. Subsequent procedures will be established to first purify the materials and to characterize their structures. TGA, in conjunction with mass spectroscopy, will be used to verify mass loss vs. temperature as well as to identify the gas decomposition products as a function of temperature.

Results

LiNH₂/MgH₂ Kinetics

Previously, this study reported the charge and discharge profiles for precursor materials LiNH₂ and MgH₂ in a 1:1 mole ratio with 0.67 mol% TiCl₃

catalyst loading. These profiles were measured using a Sievert's apparatus under isothermal conditions. Previous MHCoE work [1,2] on this material indicated the presence of a LiMgN phase which was not confirmed in this work. Instead, a Mg₃N₂ or partially substituted (Li,Mg)₃N₂ phase was detected using powder XRD. Other researchers have observed the presence of alternate discharge products in this system [8]. A standard discharge condition of 280°C into a nominal 1 bar back pressure for ~8 hours was selected (D-280°C/1 bar/8 hrs), along with a standard charge condition of 180°C under a nominal 150 bar pressure for 6 hrs (D-180°C/150 bar/6 hrs). These conditions were selected to reach maximum charge and discharge capacities in a single work day and will be used to compare differing compositions, catalysts etc.

A traditional kinetic analysis on the 0.67 mol% TiCl₃ doped material yielded an activation energy for hydrogen discharge of ~60 kJ/mol. A Johnson-Mehl-Avrami approximation was performed that indicated the reaction mechanism changes at least once during discharge cycle. Preliminary isoconversional kinetic analysis is consistent with the Johnson-Mehl-Avrami analysis, indicating that the discharge reaction occurs via a multi-step mechanism.

In order to investigate the effect of higher catalyst loading, material was prepared at the stoichiometric ratio of LiNH₂:MgH₂ (1:1) with 4 mol% TiCl₃ added. The data for the two catalyst loadings are shown in Table 1. The charge and discharge rates are calculated on a mass-specific basis and an extrapolated system basis, assuming a 72 kg hydride bed would be required to store 5 kg of hydrogen for an automotive application. From these data, it is observed that the catalyst loading has little effect on the charging rate and temperature has only a moderate effect on the charging rate. A maximum in charging rate is observed at approximately 180°C. A strong effect of charging pressure on the charge rate is observed, with a 500% increase in charging rate between 70 bar and 150 bar. The charging times associated with these rates required to reach 80% of the full charging capacity for a given experiment are ~30 min, which is within an order of magnitude of the DOE technical target for a charging time of 3 minutes.

The effect of catalyst loading on discharge time was also examined. The catalyst loading has a significant effect on the discharge rate of the material, with a 2.5x charging rate increase with a 2.5x increase in catalyst loading. This suggests that while catalyst loading may not be a significant parameter for the charging rates, it is very important to understand and optimize the catalyst for the discharge rate. The projected rate of discharge for the scaled-up bed approximation is ~1.8 gH₂/sec, which is the same order of magnitude as the requirement of a 80-100 kW fuel cell.

TABLE 1. Summary of charge and discharge data for $\text{LiNH}_2\text{:MgH}_2$ (1:1) as a function of TiCl_3 loading, temperature and pressure.

0.66 mol% TiCl_3 (4 wt%)		Rate [g H_2 / (s·g _s)]	Rate 72 kg bed	4 mol% TiCl_3 (13.7 wt%)		Rate [g H_2 / (s·g _s)]	Rate 72 kg bed
P	150 bar	Charge		P	150 bar	Charge	
Temp	160°C	2.0×10^{-5}	1.43	Temp	160°C	1.9×10^{-5}	1.40
	180°C	2.4×10^{-5}	1.73		180°C	2.5×10^{-5}	1.80
	200°C	1.9×10^{-5}	1.38		200°C	2.3×10^{-5}	1.68
	220°C	1.7×10^{-5}	1.26				
Temp	160°C	Charge		Temp	180°C	Charge	
P	70 bar	4.6×10^{-6}	0.330	P	70 bar	6.0×10^{-6}	0.430
	100 bar	1.2×10^{-5}	0.811		100 bar	1.2×10^{-5}	0.882
	150 bar	2.0×10^{-5}	1.43		150 bar	2.5×10^{-5}	1.80
Discharge				Discharge			
T = 280°C	P = 1 bar	1.0×10^{-5}	0.737	T = 280°C	P = 1 bar	2.4×10^{-5}	1.72

$\text{Ca}(\text{BH}_4)_2/\text{LiNH}_2$ (1:2 mol) Procedures

Calcium borohydride was purchased from Aldrich as an adduct $\text{Ca}(\text{BH}_4)_2 \cdot 2(\text{tetrahydrofuran})$. Tetrahydrofuran was evacuated at 180°C for 8 hrs. LiNH_2 (95% purity) was purchased from Aldrich and used as-is. Inside the glove box, LiNH_2 (0.329 g, 2.0 mol) was combined with $\text{Ca}(\text{BH}_4)_2$ (0.500 g, 1.0 mol) into a stainless-steel ball milling vessel along with eight small (0.635 cm diameter) stainless-steel balls. The vessel was put on a Fritsch planetary mill for four 30 min cycles. A white opaque solid was recovered.

Results and Discussion

The ball milled mixture between 2 moles of LiNH_2 and 1 mole of the undoped $\text{Ca}(\text{BH}_4)_2$ showed a main dehydriding event at a more favorable temperature between 250-350°C. Further TGA analyses of the lone LiNH_2 and lone $\text{Ca}(\text{BH}_4)_2$ will be conducted to see whether or not there is a decrease in dehydriding temperature by mixing LiNH_2 and $\text{Ca}(\text{BH}_4)_2$.

Powder XRD pattern of the mixture between LiNH_2 and $\text{Ca}(\text{BH}_4)_2$ (2:1 mole) revealed that the mixture is largely amorphous. All the attendant peaks of the reactants LiNH_2 and $\text{Ca}(\text{BH}_4)_2$ have disappeared which may indicate that a reaction have taken place. Further characterization by FTIR and Raman spectroscopy will be done to see the extent of the N-H stretching shift which is caused by the rearrangement of the constituent hydrides in a newly formed compound.

Thermally programmed desorption analysis of the mixture (2 LiNH_2 + $\text{Ca}(\text{BH}_4)_2$) by Seivert's apparatus revealed that there is one main dehydriding event which begins at 170°C, accelerates at 250°C and ends at 310°C. The dehydriding temperature is approximately 100°C

less than that of the $\text{Ca}(\text{BH}_4)_2$ by itself (Figure 1). Mass spectrometry analysis of the discharged gas by residual gas analyzer revealed that hydrogen was the main gas released.

Conclusions

- Desorption products in all cases considered appear to be the same (mixture of LiCl , Mg_3N_2 , LiMgN and a minor amount of an unidentified phase [$<5\%$]).
- Increased catalyst loading significantly affects H_2 discharge rate.
- Ti^{+3} is a powerful catalyst for desorption but has minimal effect in absorption.
- A characteristic charging time (τ_{80}) of 30 minutes, calculated for the isothermal charging results, is faster than those presented elsewhere in the literature.

FIGURE 1. Thermally programmed desorption results of (A) a mixture between $\text{Ca}(\text{BH}_4)_2$ + 2 LiNH_2 (B) LiNH_2 and (C) $\text{Ca}(\text{BH}_4)_2$.

- Gravimetric storage density for the isothermal measurements is lower than that reported by Lu et al. [1] for the same material (~6.66 wt% versus ~8.0 wt%).
- Ball milling LiNH_2 and $\text{Ca}(\text{BH}_4)_2$ (2:1 mole ratio) gave an amorphous phase. $\text{Li}_x\text{Ca}(\text{BH}_4)_x(\text{NH}_2)_y$ having a dehydriding temperature at 100°C lower than component $\text{Ca}(\text{BH}_4)_2$.

Future Directions

- Test other catalysts to render faster kinetics, lower temperatures of operation (e.g. VCl_3 , NiCl_3 , FeCl_3 ...).
- Analyze the purity of the discharged H_2 as a function of temperature using a residual gas analyzer and FTIR.
- Identify structures and compositions of $\text{Li}_x\text{Ca}(\text{BH}_4)_x(\text{NH}_2)_y$.
- Synthesize and characterize $\text{LiMg}(\text{BH}_4)_x(\text{NH}_2)_y$ and $\text{LiCa}(\text{BH}_4)_x(\text{NH}_2)_y$.
- Elucidate the origin of the reduction in dehydriding temperature.
- Synthesize $\text{Mg}(\text{NH}_2)_2$ and $\text{Ca}(\text{NH}_2)_2$ as precursors for synthesis of $\text{LiMg}(\text{BH}_4)_x(\text{NH}_2)_y$ and $\text{LiCa}(\text{BH}_4)_x(\text{NH}_2)_y$.

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IV.A.1q Synthesis of Nanophase Materials for Thermodynamically Tuned Reversible Hydrogen Storage

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- Sonjong Hwang, Caltech, Pasadena, CA
- J. Reiter, Jet Propulsion Laboratory (JPL), Pasadena, CA

Project Start Date: October 1, 2004

Project End Date: January 31, 2010

Objectives

- To understand as to whether thermodynamically tractable reactions based on hydride destabilization that should be reversible but appear not to be, are kinetically limited.
- To address short hydrogenation times associated with refueling, that will require short solid-state and gas-solid diffusion path lengths.
- To address the problems associated with large, light-metal-hydride enthalpies (hydrogen fueling/refueling temperatures) and develop strategies to address thermodynamic issues surrounding the use of these materials through hydride destabilization. Systems of interest determined through “theoretical screening” by Center partner members.
- To understand issues related to grain growth and surface/interface energies, vital in order to understand the kinetics of hydrogenation/dehydrogenation reactions.
- To follow up on previously studied reactions with phase identification via X-ray diffraction (XRD), nuclear magnetic resonance (NMR) and transmission electron microscopy.

Technical Barriers

This project addresses the following technical barriers from the Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) System Weight and Volume
- (P) Lack of Understanding of Hydrogen Physisorption and Chemisorption
- (Q) Reproducibility of Performance

Technical Targets

Data are typically reported as gravimetric densities on a materials basis only. The contribution to the system weights from the tank walls and tubing are not considered in our values whereas the 2010 targets for gravimetric and volumetric capacity are targeted on system’s basis of 6% and 0.045 kg/L, respectively.

Accomplishments

Motivated by the more recent work of Alapati, Johnson and Sholl, the systems that we have synthesized and analyzed over the past year are:

- $\text{TiH}_2 + 2\text{LiBH}_4 \rightarrow \text{TiB}_2 + 2\text{LiH} + 4\text{H}_2$ 8.6 wt% and 22 kJ/mole H_2 theoretical, and
- $\text{CaH}_2 + 6\text{LiBH}_4 \rightarrow \text{CaB}_6 + 6\text{LiH} + 10\text{H}_2$, analogues where Sr (9.1 wt%) and Ba have been substituted for Ca.
- X-ray and NMR analysis of the destabilization systems above.
- Wetting analysis of reactants of prospective use with scaffolds that minimize diffusion path lengths.
- Evaluation of reaction pathways where closo-borane intermediate phases are formed.
- Continuation of transmission electron microscopic examination of phase distributions in Mg incorporated into aerogels.

Introduction

Candidate hydride destabilization systems of technological interest must meet the requirements of generating high gravimetric densities of hydrogen and do so at reaction enthalpy values of between 30 and 40 kJ/mole for tractable thermal management of storage systems. While thermochemical databases have been of

use in exploring initial candidate systems, we have relied on the efforts of the Metal Hydride Center of Excellence theory group [1] who have calculated formation and reaction enthalpies of systems that fall within the requisite thermodynamic boundaries.

Reaction kinetics also represent a critical gauge of engineering utility and our approach is to work with the most promising candidates as determined by thermodynamics, and to study the kinetics of hydrogen release. Kinetics will be dominated by solid-state diffusion rates in hydride destabilization systems and both volumetric and analytical techniques are required in order to understand reaction pathways.

Approach

We have been evaluating the most promising hydride destabilization systems using Sieverts volumetric techniques to determine actual gravimetric hydrogen release and the associated kinetics aided by standard catalysts. We have been working with spectroscopic analyses like XRD diffraction and NMR in collaboration with JPL (see report from J. Reiter of JPL) and Sonjong Hwang of the Caltech NMR facility in order to gain insights into these systems.

Results

In Figure 1 we show the results of the reaction $\text{TiH}_2 + 2\text{LiBH}_4 \rightarrow \text{TiB}_2 + 2\text{LiH} + 4\text{H}_2$, where: $\Delta U_{\text{OK}} = 22.2 \text{ kJ/mol H}_2$ (8.6 wt% capacity). In spite of the compelling thermodynamics of this reaction which made this a system of promise, our desorption measurements of ball milled powders taken over a 95-hour run showed no reaction. The lack of reactivity was confirmed by powder XRD and by NMR. Apparently, the stability of TiH_2 and TiB_2 do not allow activation under these conditions or kinetics are very slow for desired reaction.

Figure 2 shows the results of the destabilization reaction $\text{SrH}_2 + 6\text{LiBH}_4 \rightarrow \text{SrB}_6 + 6\text{LiH} + 10\text{H}_2$, a 9 wt% system. This reaction was not calculated specifically by Alapati, Sholl and Johnson but the use of higher Z alkaline earth elements was motivated by the possibility that larger electron densities might translate to weaker bonds and better thermodynamics and/or kinetics. Our initial work shows that after desorption at 350°C , sample changes to strong green colored powder. Powder XRD of desorption product shows unanticipated reaction paths producing phases, including: a LiSrH_3 trivalent, SrB_6 as noted by very broad peaks meaning a small sized reaction phase, unreacted LiBH_4 and LiH . This reaction

FIGURE 1. Kinetic desorption measurement from the $\text{TiH}_2 + 2\text{LiBH}_4 \rightarrow \text{TiB}_2 + 2\text{LiH} + 4\text{H}_2$ up to 350°C shown in upper left. XRD data from as milled and reacted sample shown in upper right. ^1H MAS NMR spectra shown at lower left and the same ^1H MAS NMR spectra as, blown up to show the TiH_2 peaks at -159 ppm in lower right.

FIGURE 2. The $\text{SrH}_2 + 6\text{LiBH}_4 \rightarrow \text{SrB}_6 + 6\text{LiH} + 10\text{H}_2$ system has reacted at 350°C as shown by the color change in the upper left. X-ray data in the upper right shows intermediate reaction product phases that were formed.

yielded 3.5 wt% H_2 initially but further assessment of reaction pathway kinetics is still needed.

Figure 3 shows an example of some of the wetting experiments that we have been performing in assessing the extent of wet-ability/reactivity for the purposes of setting up destabilization reactions in carbon aerogel scaffolds. Assessing surface reactivity will be crucial in promoting destabilization reactions in carbon aerogel scaffolds. In an effort to determine the intrinsic reactivity of constituents that might affect the ability to incorporate hydrides into scaffolds and ultimately, the kinetics of destabilization, wetting experiments of LiBH_4 were performed over compressed disks of MgH_2 and TiH_2 . In the case of LiBH_4 over MgH_2 , we can see the poor reactivity between these phases as evidenced by the “beading” of the LiBH_4 on the surface of the MgH_2 .

Figure 4 shows our efforts at improving the spatial resolution of MgH_2 that has been infiltrated into an aerogel. We have employed energy filtered imaging, using an energy filter located on our TF20 transmission electron microscope and using the $\text{Mg L}_{2,3}$ edge as an image source. The zero loss images of the microstructure are shown in the upper set and the corresponding Mg images are shown in the lower set. The Mg images (bright features) suggest that Mg is fairly uniformly distributed in the aerogel structure. There is though, possibility that the images are dominated by thickness effects. In the future we plan avoid this by the use plasmon imaging to better resolve the differences in electron density of the hydride phase (14 eV) and that are distinct from the metal (10 eV), oxide (22 eV) and carbon (25 eV) signatures.

Conclusions and Future Directions

- The destabilization reactions that we have concentrated on so far have limited hydrogen release, due to either to the poor reactivity of the species (in spite of favorable thermodynamics),

FIGURE 3. Images above show melting behavior of LiBH_4 over a milled and compacted MgH_2 powder. The initial LiBH_4 before heating is shown on the left and upon heating, forms a bead with a large contact angle, indicating a poor reactivity between these two phases.

FIGURE 4. Energy filtered images of Mg incorporation into carbon aerogel. Zero loss images of the microstructure are shown in the upper set and the corresponding Mg images are shown in the lower set.

which can be due to high formation enthalpies of one or more of the reacting species. Promoting reactivity through careful control of wetting behavior will better enable us to promote constituent reactivity.

- Formation of intermediate compounds, not predicted by has also been a problem that we have been attempting to work around. The stable closo-borane structures have appeared as intermediate phases when borohydrides have been used as a reactant. Using conditions that suppress the formation of these stable phases will be vital in our continuing work in this area.
- Basic wetting behavior studies have been an instrumental first step in determining the viability of destabilization reactions.
- We plan to explore schemes for promoting surface reactivity as we work to complete our effort in this area.

FY 2009 Publications/Presentations

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2. "Synthesis and hydrogen storage properties of MgH_2 incorporated carbon aerogel scaffold," Shu Zhang, Adam F Gross, Sky L Van Atta, Maribel Lopez, Ping Liu, Channing C Ahn, John J Vajo and Craig M Jensen, *Nanotechnology* (2009).
3. " $\text{LiSc}(\text{BH}_4)_4$ as a Hydrogen Storage Material: Multinuclear High Resolution Solid State NMR and First-Principles Density Functional Theory Studies" Kim, C. et al. submitted to *J. Phys. Chem. C*. (Feb 2009).

Presentations

1. "Vehicular Hydrogen Storage with Ad(b)sorbent Materials," C. Ahn, APS Energy Research Workshop Program and Hydrogen Focus Topic Symposium chair, *American Physical Society, March 2009, Natl. Meeting, Pittsburgh*.

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IV.A.1r Lightweight Metal Hydrides for Hydrogen Storage

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Contract Number: DE-FC3605GO15062

Project Start Date: January 1, 2005
Project End Date: August 31, 2011

Objectives

The objective of this project is to develop a high-capacity lightweight hydride for reversible vehicular hydrogen storage, capable of meeting or exceeding the 2010 DOE/FreedomCAR targets. The current focus of the project is on Mg-containing borohydrides and their complexes as well as aluminoborane compounds which have very high capacities and attractive properties. The key is to make them reversible. To accomplish this, we are working on detailed characterization of their decomposition mechanism and their amine complexes as well as new borohydrides.

Technical Barriers

This project addresses the following technical barriers from the Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Multi-Year Research, Development and Demonstration Plan:

- (D) Durability/Operability
- (E) Charging/Discharging Rates
- (J) Thermal Management
- (P) Lack of Understanding of Hydrogen Physisorption and Chemisorption

Technical Targets

This project is conducting fundamental studies of the decomposition mechanism of $\text{Mg}(\text{BH}_4)_2$. Insights gained from these studies will be applied toward the design and synthesis of hydrogen storage materials that meet the following DOE 2010 hydrogen storage targets:

- Cost: \$4/kWh net
- Specific energy: 1.5 kWh/kg
- Energy density: 0.9 kWh/L

Accomplishments

- Explored the synthesis of pure $\text{MgB}_{12}\text{H}_{12}$ in order to study the stability of this very important intermediate phase that is key to the reversibility of $\text{Mg}(\text{BH}_4)_2$. We found that the literature claim of anhydrous $\text{MgB}_{12}\text{H}_{12}$ synthesis was incorrect. We studied the stability H_2O and OH complexes of $\text{MgB}_{12}\text{H}_{12}$ and gained clear understanding of their relative stabilities.
- Synthesized $(\text{NH}_4)_2\text{B}_{12}\text{H}_{12}$, $\text{Mg}(\text{NH}_3)_6\text{B}_{12}\text{H}_{12}$ and other compounds during the synthesis of $\text{MgB}_{12}\text{H}_{12}$ and we are studying their properties to explore suitability for hydrogen storage.
- Explored synthesis of analogy compounds $(\text{NH}_4)_2\text{B}_{10}\text{H}_{10}$ and $\text{Mg}(\text{NH}_3)_6\text{B}_{10}\text{H}_{10}$ based on a consideration that the $\text{B}_{10}\text{H}_{10}$ compounds may be less stable than their $\text{B}_{12}\text{H}_{12}$ counterparts – thus potentially more suitable for hydrogen storage.
- Studied a “new” class of hydrides – aluminoborane compounds for hydrogen storage in collaboration with Oak Ridge National Laboratory (ORNL), the Jet Propulsion Laboratory (JPL), and the California Institute of Technology (Caltech). These compounds such as $\text{AlB}_4\text{H}_{11}$ have low desorption temperatures, high wt% hydrogen, low amounts of diborane, and at least partial reversibility at mild conditions (200°C, 90 bar H_2).
- Synthesized $\text{Li}_2\text{B}_{12}\text{H}_{12}$ and provided the material to Metal Hydride Center of Excellence partners for encapsulation into aerogels and other studies.
- Re-synthesized $\text{Mg}(\text{BH}_4)_2(\text{NH}_3)_2$ and have gained much better understanding of its desorption process via high-resolution nuclear magnetic resonance (NMR) studies in collaboration with ORNL, JPL and Caltech.

Introduction

The U.S. Department of Energy (DOE) defines on-board hydrogen storage for mobile vehicles as a “Grand Challenge”. It is one of the biggest hurdles to the implementation of hydrogen-powered vehicles. Metal hydrides have the advantages of the highest volumetric density, relatively low working pressure, and reasonable working temperature range. The disadvantage of current reversible hydrides is a significant weight penalty. Metal borohydrides have among the highest gravimetric hydrogen storage capacities with the potential to meet the DOE gravimetric density targets and to offset the system weight penalties. However, desorption temperature, reversibility and diborane formation during desorption are challenging issues for these materials. This project attempts to develop a high-capacity lightweight hydride for reversible vehicular hydrogen storage, capable of meeting or exceeding the 2010 DOE/FreedomCAR targets.

Approach

- Explore two classes of materials: Mg-containing borohydrides and aluminoborane compounds such as $\text{AlB}_4\text{H}_{11}$ and their amine complexes.
- Study the crystal structures and the decomposition mechanisms using multiple techniques such as interrupted pressure-concentration-temperature tests, NMR, infrared (IR), differential scanning calorimetry (DSC), and residual gas analysis.
- Develop reversibility strategy from detailed mechanistic understanding of the complex desorption processes (such understanding is crucial for reversibility of all borohydrides);
- Synthesize new hydrides and complexes in collaboration with ORNL, JPL, Caltech, Sandia National Laboratories, and the National Institute of Standards and Technology (NIST).

Results

Our previous results clearly showed that during decomposition of $\text{Mg}(\text{BH}_4)_2$, an intermediate phase $\text{MgB}_{12}\text{H}_{12}$ appears and this phase is believed to be detrimental to reversibility [1-3]. In order to devise a viable reversibility strategy, it is very important to understand the properties of this phase. Thus, we decided to synthesize the pure compound $\text{MgB}_{12}\text{H}_{12}$ for detailed characterization. A literature reported procedure was followed and the intended product was obtained [4]. However, when NMR was performed on the powders, it was clear that the product still had H_2O attached to it. A carefully examination of the published thermogravimetric analysis (TGA) curve clearly showed that the authors made a mistake in computing the weight loss and there should be three H_2O molecules

still attached to the compound. Thus, the claimed anhydrous $\text{MgB}_{12}\text{H}_{12}$ was never really synthesized. Several different ways were attempted to remove the three residual H_2O molecules, but none of them was completely successful. For instance, the powders were heated up to 900°C ; there was still OH signals in the IR spectrum. A study was subsequently performed using both TGA and NMR to monitor the loss of H_2O and H_2 from $\text{Mg}(\text{H}_2\text{O})_6\text{B}_{12}\text{H}_{12} \cdot 6\text{H}_2\text{O}$ to $\text{Mg}(\text{H}_2\text{O})_6\text{B}_{12}\text{H}_{12}$ to $\text{Mg}(\text{H}_2\text{O})_3\text{B}_{12}\text{H}_{12}$ to $\text{Mg}(\mu\text{-OH})_3\text{B}_{12}\text{H}_x$. A manuscript is in preparation to report the results in detail.

During the process of synthesizing anhydrous $\text{MgB}_{12}\text{H}_{12}$, an attempt was made to use NH_3 to replace the residual H_2O in $\text{Mg}(\text{H}_2\text{O})_6\text{B}_{12}\text{H}_{12}$. The replacement was successful and the corresponding amine complex $\text{Mg}(\text{NH}_3)_6\text{B}_{12}\text{H}_{12}$ was obtained. This compound decomposes with an endothermic peak in the DSC curve (Figure 1) and it has very high hydrogen content. We are studying it as a potential hydrogen storage material. An attempt was made to grow a single crystal of $\text{Mg}(\text{NH}_3)_6\text{B}_{12}\text{H}_{12}$ in CH_3OH for crystal structure identification. The obtained single crystal was found to be $\text{Mg}(\text{CH}_3\text{OH})_6\text{B}_{12}\text{H}_{12} \cdot 6\text{CH}_3\text{OH}$. Thus CH_3OH was able to replace NH_3 in $\text{Mg}(\text{NH}_3)_6\text{B}_{12}\text{H}_{12}$. Powders of $\text{Mg}(\text{NH}_3)_6\text{B}_{12}\text{H}_{12}$ was sent to NIST (Dr. J.H. Her) for crystal structure analysis using both X-ray diffraction (XRD) and neutron diffraction.

In a separate route to anhydrous $\text{MgB}_{12}\text{H}_{12}$, we first synthesized $(\text{H}_3\text{O})_2\text{B}_{12}\text{H}_{12}$ from $\text{Cs}_2\text{B}_{12}\text{H}_{12}$. Subsequent NH_3 treatment of $(\text{H}_3\text{O})_2\text{B}_{12}\text{H}_{12}$ resulted in a pure $(\text{NH}_4)_2\text{B}_{12}\text{H}_{12}$ compound. Its DSC curve also showed an endothermic peak and the desorbed gas was very likely hydrogen – careful tests are in progress. Thus, this compound is also an attractive candidate for hydrogen storage. We were able to grow a single crystal of this compound and have refined its crystal structure as shown in Figure 2. Careful study of its properties is currently underway. We are ball milling $(\text{NH}_4)_2\text{B}_{12}\text{H}_{12}$ with MgH_2 to try to make $\text{MgB}_{12}\text{H}_{12}$. This process is H_2O free

FIGURE 1. DSC Curve of $\text{Mg}(\text{NH}_3)_6\text{B}_{12}\text{H}_{12}$ Showing Endothermic Desorption

FIGURE 2. Crystal structure of $(\text{NH}_4)_2\text{B}_{10}\text{H}_{12}$ based on single crystal XRD showing the $\text{B}_{10}\text{H}_{10}$ cage sits in the middle of a cubic NH_4 lattice.

and OH free, thus we hope to be able to make anhydrous $\text{MgB}_{12}\text{H}_{12}$.

Experience indicates that $\text{MB}_{10}\text{H}_{10}$ compounds are usually less stable than the analogy $\text{MB}_{12}\text{H}_{12}$, thus $\text{MB}_{10}\text{H}_{10}$ compounds may be good candidates for hydrogen storage considering that $\text{MgB}_{12}\text{H}_{12}$ is too stable. Attempts to synthesize anhydrous $\text{MB}_{10}\text{H}_{10}$ faced a similar hurdle as the synthesis of $\text{MgB}_{12}\text{H}_{12}$: difficulty to remove the $\text{H}_2\text{O}/\text{OH}$. In the process, we made $\text{Mg}(\text{H}_2\text{O})_6\text{B}_{10}\text{H}_{10} \cdot 4\text{H}_2\text{O}$ and $\text{Mg}(\text{H}_2\text{O})_6\text{B}_{10}\text{H}_{10}$ compounds. We were able to identify the crystal structure of the first compound. Powders of the second compound were also sent to NIST for structure identification. $\text{Mg}(\text{H}_2\text{O})_6\text{B}_{10}\text{H}_{10} \cdot 4\text{H}_2\text{O}$ was synthesized in water by ion exchange method by converting $[\text{NEt}_3\text{H}]_2[\text{B}_{10}\text{H}_{10}]$ to the acid form and reacting the acid with MgCO_3 . The product was characterized by DSC, NMR, IR and single crystal X-ray diffraction. Efforts to replace the water molecule from $\text{Mg}(\text{H}_2\text{O})_6\text{B}_{10}\text{H}_{10}$ with ammonia resulted only in partial ammonia substitution. Also, $(\text{NH}_4)_2\text{B}_{10}\text{H}_{10} \cdot 1.5\text{H}_2\text{O}$ was synthesized by the reaction of $[\text{H}_3\text{O}]_2[\text{B}_{10}\text{H}_{10}]$ with ammonia gas in water solution. The product was characterized by DSC, TGA, NMR, IR and single crystal XRD. The water containing compound $(\text{NH}_4)_2\text{B}_{10}\text{H}_{10} \cdot 1.5\text{H}_2\text{O}$ was heated at 70°C for 2 hours to give $(\text{NH}_4)_2\text{B}_{10}\text{H}_{10}$ as evident from the IR spectrum. The XRD pattern of anhydrous $(\text{NH}_4)_2\text{B}_{10}\text{H}_{10}$ is shown in Figure 3. Heating of $(\text{NH}_4)_2\text{B}_{10}\text{H}_{10}$ at 70°C for 2 hours resulted in no change in the $[\text{B}_{10}\text{H}_{10}]^{2-}$ boron structure, but heating at 130°C for 2 hours resulted in conversion of small amount of $[\text{B}_{10}\text{H}_{10}]^{2-}$ to $[\text{B}_{12}\text{H}_{12}]^{2-}$. Heating at 250°C resulted in change of color from white to yellow brown and $[\text{B}_{12}\text{H}_{12}]^{2-}$ formation from ^{11}B NMR.

FIGURE 3. XRD Pattern of Anhydrous $(\text{NH}_4)_2\text{B}_{10}\text{H}_{10}$

More efforts are under way to heat the anhydrous product $((\text{NH}_4)_2\text{B}_{10}\text{H}_{10})$ at different temperatures and characterize the heated residue and gaseous products.

In order to be prepared for a comparative study of the relative stability of $\text{MB}_{12}\text{H}_{12}$ compounds ($\text{M} = \text{Li}, \text{Mg}, \text{Na}, \text{Ca}$), we synthesized $\text{Li}_2\text{B}_{12}\text{H}_{12}$ following a literature route. $\text{Li}_2\text{B}_{12}\text{H}_{12} \cdot 7\text{H}_2\text{O}$ was first prepared by cation exchange. Anhydrous $\text{Li}_2\text{B}_{12}\text{H}_{12}$ was obtained by heating the compound at 250°C under vacuum for 12 hours. (We provided gram quantity $\text{Li}_2\text{B}_{12}\text{H}_{12}$ to HRL for nano-framework encapsulation.) We studied the anhydrous $\text{Li}_2\text{B}_{12}\text{H}_{12}$ using DSC, XRD, and NMR. The ammine complex then was synthesized by condensing ammonia onto anhydrous $\text{Li}_2\text{B}_{12}\text{H}_{12}$. The complex was soluble in tetrahydrofuran (THF) as indicated by boron-NMR. Two types of single crystals from the THF solution were analyzed using XRD. The first batch of single crystals were picked out from the THF solution after 24 hours, the second were picked out after one week. The structure derived from the single-crystal XRD shows that the first batch of crystals is $\text{Li}_2\text{B}_{12}\text{H}_{12} \cdot 7\text{NH}_3$. There are two types of Li cations, one coordinated by three ammonias, the other four ammonias. The second batch of crystals was identified as $\text{Li}_2\text{B}_{12}\text{H}_{12} \cdot 6\text{THF}$. Thus, the $\text{Li}_2\text{B}_{12}\text{H}_{12} \cdot 7\text{NH}_3$ was only stable in the THF solution for a limited amount of time. After one week, it transformed into $\text{Li}_2\text{B}_{12}\text{H}_{12} \cdot 6\text{THF}$. Ammonia was replaced by THF completely. In this compound, both Li cations are identical, each coordinated by three THFs. The boron cage was connected to Li cations. TGA and NMR study shows that $\text{Li}_2\text{B}_{12}\text{H}_{12} \cdot 7\text{NH}_3$ decomposes by giving off NH_3 instead of H_2 , thus it is not a viable candidate for hydrogen storage.

$\text{Mg}(\text{B}_3\text{H}_8)_2$ was synthesized as a precursor for chemical vapor deposition of MgB_2 [5]. The authors reported a melting and desorption temperature of 120°C , thus it can potentially be an interesting candidate for hydrogen storage material if it is reversible. The synthesis of this compound requires the use of NaB_3H_8 as a starting material. NaB_3H_8 will also be a useful compound for a comparison study of the stability of MB_3H_8 compounds ($\text{M} = \text{Li}, \text{Mg}, \text{Na}, \text{and Ca}$). In this

regards, we have developed new method for better synthesis of NaB_3H_8 .

In collaboration with JPL and Caltech, we employed high resolution NMR to compare the desorption products of $\text{Mg}(\text{BH}_4)_2$, $\text{Mg}(\text{BH}_4)_2(\text{NH}_3)_2$, and $\text{Mg}(\text{BH}_4)_2(\text{NH}_3)_2 + n\text{LiBH}_4$ ($n = 1, 2$). Disordered boron-nitrogen is identified as the initial desorption product of $\text{Mg}(\text{BH}_4)_2(\text{NH}_3)_2$. $[\text{B}_{12}\text{H}_{12}]^{2-}$ anion is the primary intermediate species during desorption of LiBH_4 , $\text{Mg}(\text{BH}_4)_2$, and $\text{Mg}(\text{BH}_4)_2(\text{NH}_3)_2 + n\text{LiBH}_4$ ($n = 1, 2$). A manuscript is in the process for submission for publication.

Attempts have been made to synthesize the complex metal hydride $\text{Mg}(\text{BH}_4)(\text{AlH}_4)$ using modified procedures reported by Ashby and Goel [6]. Earlier preliminary work at General Electric on $\text{Mg}(\text{BH}_4)(\text{AlH}_4)$ synthesis didn't separate it from the by-product salt. However, the desorption temperature was significantly lower than that of $\text{Mg}(\text{BH}_4)_2$. We have tested four different methods trying to make the pure $\text{Mg}(\text{BH}_4)(\text{AlH}_4)$ compound. $\text{Mg}(\text{BH}_4)(\text{AlH}_4)\cdot\text{THF}$ was found to decompose slowly at room temperature to very nice colorless crystals of $\text{Mg}(\text{AlH}_4)_2\cdot 4\text{THF}$ and $\text{Mg}(\text{BH}_4)_2\cdot 3\text{THF}$ powders. Characterization of the other products is still in progress.

Our work on aluminoborane compounds such as $\text{AlB}_4\text{H}_{11}$ was on hold waiting for a new batch of materials from ORNL. The new batch has now arrived at OSU and more exploration of its reversibility conditions is currently underway.

We built a specialized glovebox around a Mettler Toledo high-pressure DSC unit to allow inert transfer of sample from the large glovebox to the DSC. This DSC unit will be the workhorse equipment for us since heat absorption and desorption (thermodynamics) is the key indicator of potential reversibility.

Conclusions and Future Directions

The OSU hydrogen storage materials research team has synthesized and tested several new compounds for hydrogen storage. This was made possible by the availability of four vacuum wet-chemistry synthesis lines in Prof. Sheldon Shore's laboratory, a group of dedicated researchers, the unique boron chemistry expertise in the group, and a dedicated hydride testing facility established in Dr. J.-C. Zhao's laboratory. Close collaboration with ORNL, JPL, Caltech, and NIST made possible effective synthesis and characterization of these compounds.

The materials we are synthesizing and studying including $\text{Mg}(\text{BH}_4)_2$, $\text{Mg}(\text{BH}_4)_2(\text{NH}_3)_2$, $\text{Mg}(\text{AlH}_4)(\text{BH}_4)$, $\text{Mg}(\text{NH}_3)_6\text{B}_{12}\text{H}_{12}$, $(\text{NH}_4)_2\text{B}_{12}\text{H}_{12}$, $\text{Mg}(\text{CH}_3\text{OH})_6\text{B}_{12}\text{H}_{12}$, $\text{Mg}(\text{H}_2\text{O})_3(\text{CH}_3\text{OH})_3\text{B}_{12}\text{H}_{12}$, $\text{Li}_2\text{B}_{12}\text{H}_{12}(\text{NH}_3)_7$, $(\text{NH}_4)_2\text{B}_{10}\text{H}_{10}$, $\text{Na}(\text{NH}_3)_x\text{B}_{12}\text{H}_{12}$, $\text{Mg}(\text{H}_2\text{O})_6\text{B}_{10}\text{H}_{10}$,

$\text{Mg}(\text{NH}_3)_x\text{B}_{10}\text{H}_{10}$, $\text{AlB}_4\text{H}_{11}$, and $\text{Mg}(\text{B}_3\text{H}_8)_2$. Several of these compounds are new compounds that were not reported before. A few of these compounds showed endothermic desorption at low temperatures, thus they are good candidates for further study as potential hydrogen storage materials. The following compounds are very worthy of further studies: $\text{Mg}(\text{BH}_4)_2$, $\text{Mg}(\text{AlH}_4)(\text{BH}_4)$, $\text{Mg}(\text{NH}_3)_6\text{B}_{12}\text{H}_{12}$, $(\text{NH}_4)_2\text{B}_{12}\text{H}_{12}$, $(\text{NH}_4)_2\text{B}_{10}\text{H}_{10}$, $\text{Mg}(\text{NH}_3)_x\text{B}_{10}\text{H}_{10}$, $\text{AlB}_4\text{H}_{11}$, and $\text{Mg}(\text{B}_3\text{H}_8)_2$.

We will perform more detailed study of these compounds for hydrogen storage in collaboration with ORNL, JPL/Caltech, Sandia, and NIST. We will focus on more promising candidates as the properties of these compounds are tested.

Special Recognitions & Awards/Patents Issued

1. J.-C. Zhao was named by the National Academy of Engineering (NAE) as one of eight-two brightest young engineers to attend the NAE 2008 Frontier of Engineering Symposium: <http://www8.nationalacademies.org/onpinews/newsitem.aspx?RecordID=06172008>

FY 2009 Publications/Presentations

1. MH2008 International Conference on Hydrogen-Metal Systems, Reykjavik, Iceland, June 24–28, 2008, “ $\text{Mg}(\text{BH}_4)_2$ and Its Complexes for Hydrogen Storage”, Grigori Soloveichik, Sergei Kniajansky, Job Rijssenbeek, Yan Gao, Robert C. Bowman, Jr. and Son-Jong Hwang, J.-C. Zhao.
2. IEA Task 22 International Experts Meeting, Villa Mondragone, Italy, October 7–10, 2008. “Hydride Research at OSU”, J.-C. Zhao.
3. Lehigh University, October 14th, 2008. “Hydrogen Storage Materials” (Invited talk), J.-C. Zhao.
4. International Energy Agency (IEA) Task 22 Hydrogen Storage Experts' Meeting, The Shilla Jeju Hotel, Jeju Island, Korea, April 19-23, 2009. “Lightweight Borohydrides for Hydrogen Storage”, J.-C. Zhao*, S. Shore, X. Chen, Z. Huang, H. Kumar, T. Yisgedu, B. Billet, and J. Hoy.
5. North American Solid State Chemistry Conference, Columbus, OH, June 17–20, 2009. “Borohydrides for Hydrogen Storage”, X. Chen*, Z. Huang, H. Kumar, T. Yisgedu, B. Billet, J. Hoy, S.G. Shore, J.-C. Zhao (Poster).
6. S.-J. Hwang, R.C. Bowman, Jr., J.W. Reiter, J. Rijssenbeek, G.L. Soloveichik, J.-C. Zhao, H. Kabbour, and C.C. Ahn, “NMR Confirmation for Formation of $\text{B}_{12}\text{H}_{12}$ Complexes during Hydrogen Desorption from Metal Borohydrides”, *Journal of Physical Chemistry C*, vol. 112, p. 3164-3168 (2008).
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IV.A.2 Design of Novel Multi-Component Metal Hydride-Based Mixtures for Hydrogen Storage

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Contract Number: DE-FG36-08GO18136

Project Start Date: September 1, 2008
(Funding started February 2009)
Project End Date: July 31, 2013

Technical Barriers

This project addresses the following technical barriers from the Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (P) Lack of Understanding of Hydrogen Physisorption and Chemisorption
- (A) System Weight and Volume
- (E) Charging/Discharging Rates

Technical Targets

This project is conducting fundamental studies of novel multi-component mixtures of complex and chemical hydrides. Insights gained from these studies will be applied toward the development of hydrogen storage materials and reactions that meet the following DOE 2010 hydrogen storage targets:

- Specific energy: 1.5 kWh/kg
- Energy density: 0.8 kWh/L

Objectives

The objective of the project is to discover novel mixed hydrides for hydrogen storage, which enable the DOE 2010 system-level goals. Since prior Argonne National Laboratory/TIAX system-level modeling has shown that there will likely be a ~50% penalty on the material's gravimetric capacity due to balance-of-plant issues, our goal is to find a material that desorbs 8.5 wt% H₂ or more at temperatures below 85°C. The project will combine first-principles calculations of reaction thermodynamics and kinetics with material and catalyst synthesis, testing, and characterization.

- Three materials classes (chemical, metal/complex, physisorptive) divided into DOE Centers of Excellence.
- Our project: Combine materials from distinct categories to form novel multi-component reactions.
- Systems to be studied include mixtures of complex hydrides and chemical hydrides (e.g. LiNH₂+NH₃BH₃) and nitrogen-hydrogen-based borohydrides (e.g. Al(BH₄)₃(NH₃)₃).

Approach

The 2010 and 2015 FreedomCAR/DOE targets for hydrogen storage systems are very challenging, and cannot be met with existing materials. The vast majority of the work to date has delineated materials into various classes, e.g., complex and metal hydrides, chemical hydrides, and sorbents. However, very recent studies indicate that *mixtures* of storage materials, particularly mixtures *between various classes*, hold promise to achieve technological attributes that materials within an individual class cannot reach. Our project involves a systematic, rational approach to designing novel multicomponent mixtures of materials with fast hydrogenation/dehydrogenation kinetics and favorable thermodynamics using a combination of state-of-the-art scientific computing and experimentation. We will use the accurate predictive power of first-principles modeling to understand the thermodynamic and microscopic kinetic processes involved in hydrogen release and uptake and to design new material/catalyst systems with improved properties. Detailed characterization and atomic-scale catalysis experiments will elucidate the effect of dopants and nanoscale catalysts in achieving fast kinetics and reversibility. And, state-of-the-art storage experiments will give key

storage attributes of the investigated reactions, validate computational predictions, and help guide and improve computational methods. In sum, our approach involves a powerful blend of: 1) H_2 storage measurements and characterization, 2) state-of-the-art computational modeling, 3) detailed catalysis experiments, 4) in-depth automotive perspective.

Accomplishments

- Recently discovered a novel hydrogen storage medium that combines the $[B_{12}H_{12}]_2^-$ anion with the ammonium *complex cation* to form $(NH_4)_2B_{12}H_{12}$, ammonium dodecaboro-closo-dodecahydride, at 11.3 wt% H_2 (Figure 1). By using a combination of first-principles total energy calculations and finite-temperature phonons, with the recently-developed Grand Canonical Linear Programming approach

FIGURE 1. Crystal Structure of the $(NH_4)_2B_{12}H_{12}$ Compound

[1] we show that the thermodynamically-preferred decomposition reaction sequence for $(NH_4)_2B_{12}H_{12}$ releases all 11.3 wt% H_2 between 20-30 kJ/mol H_2 . Experimental testing of this reaction is underway.

- Currently calculating the formation energies and thermodynamic properties of all binary, ternary, quaternary, and quinary Li-Mg-B-N-H compounds from the Inorganic Crystal Structure Database. The calculated free energies will be used as inputs to the grand-canonical linear programming approach for determining reaction pathways in multinary systems.
- Refining the prototype electrostatic ground state search method for predicting crystal structures of currently unknown materials. Implementing a dramatically more efficient algorithm for finding the ground states using the recently proposed Wang-Landau Monte Carlo method. We have completed extensive tests for simple Lennard-Jones systems and are in a position now to conduct extensive searches for the crystal structures of new hydrogen storage compounds, with ammoniated borohydrides and metal-substituted derivatives of amido boranes and borohydrides as the first targets.
- Initiated a general experimental/theoretical study of the amide-borohydride mixture phase space involving reactions of the type: $X M_1(NH_2) + Y M_2(BH_4) \rightarrow M_1M_2(NH_2)_x(BH_4)_y$. First principles calculations show promising low-energy solid-state synthesis routes. Initial thermally programmed desorption-mass spectrometry data have been taken from the first series of mixtures we have investigated involving $NaNH_2 + NaBH_4$ with varying ratios of amide to borohydride.

FY 2009 Publications/Presentations

- Presentation at 2009 Hydrogen Program Annual Merit Review Meeting, C. Wolverton.

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IV.A.3 Tuneable Thermodynamics and Kinetics for Hydrogen Storage: Nanoparticle Synthesis using Ordered Polymer Templates

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- University of California, Berkeley, CA
- Lawrence Livermore National Laboratory, Livermore, CA

Project Start Date: September 30, 2008

Project End Date: September 30, 2011

(C) Efficiency

(P) Lack of Understanding of Hydrogen Physisorption and Chemisorption

Technical Targets

This project is directed toward developing hydrogen storage materials with desorption thermodynamics and kinetics that can be tuned to meet specific system requirements. The project is based on the hypothesis that confinement of metal hydrides within the chemically and geometrically well-defined pores of nanoporous framework materials such as metal-organic frameworks (MOFs) will destabilize the materials, thereby reducing their H₂ desorption temperatures and accelerating the kinetics. If successful, the project will address the following DOE technical targets, as outlined in the Hydrogen Storage Multi-Year RD&D Plan:

DOE Targets for Hydrogen Storage

Parameter	DOE 2010 Target	Project Status
Maximum delivery temperature	85°C	H ₂ desorption as low as 75°C in vacuum observed for nanoconfined NaAlH ₄ (bulk desorbs at 250°C under the same conditions)

Objectives

- Achieve tunable thermodynamics for high-gravimetric-capacity metal hydrides by creating and stabilizing nanoparticles with controlled size, composition, and properties.
- Develop synthetic routes for reactive metal nanoparticles within crystalline nanoporous materials and block copolymer templates.
- Systematically probe the effects of size and composition to determine the onset and extent of nanoscale effects on the thermodynamics and kinetics of hydrogen sorption.
- Benchmark theoretical approaches to modeling the thermodynamics metal hydride nanoparticles and develop computational tools to guide synthesis.

Technical Barriers

This project addresses the following technical barriers from the Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration (RD&D) Plan:

(A) System Weight and Volume

Accomplishments

- Developed infiltration methods for metal hydrides, e.g. NaAlH₄, MgH₂, LiBH₄, and LiH.
- Demonstrated that H₂ desorption from NaAlH₄ nanoparticles confined within MOF templates is reduced by at least 100°C, a major step toward meeting the DOE Technical Target of 85°C.
- Benchmarked density functional theory (DFT) against Quantum Monte Carlo (QMC), revealing size-dependent nonsystematic errors in H₂ desorption enthalpies. QMC confirms the lowering of temperature (1 bar) for MgH₂ nanoparticles relative to bulk.

Introduction

Some of the most attractive hydrogen storage materials, such as MgH₂, AlH₃, and LiBH₄, have unfavorable desorption thermodynamics and are either too stable (e.g. MgH₂) or too unstable (e.g. AlH₃) in

bulk form to be practical, particularly for vehicular transport applications. However, recent theoretical and experimental results indicate that decreasing particle size can substantially reduce the stability of metal hydrides, leading to lower desorption temperatures. The key challenges that must be addressed are to:

- 1) develop synthetic routes that provide controlled size and composition;
- 2) stabilize particles over time; and
- 3) develop computational tools to guide synthesis that can accurately address particle sizes spanning the micro-to-meso length scales.

This project addresses all three challenges and, if successful, will create for the first time nanoscale hydrogen storage materials with tailorable composition and size compatible with fuel-cell materials over a wide range of operating temperatures.

Approach

We are using highly ordered, chemically tailorable nanoporous templates to create particles ranging in size from <1 nm to 20 nm, the critical size range at which nanoscale effects are anticipated. These templates are infiltrated with hydride precursors or hydrides themselves, using mild synthetic routes that eliminate template degradation. The resulting template-stabilized nanoparticles, are characterized to determine particle size, composition, and desorption thermodynamics and kinetics. Validated computational modeling tools guide synthesis. This approach allows nanoparticle dimensions and hydride composition to be systematically varied, enabling the effects of nanoscale dimensions on hydride thermodynamics to be determined.

Two classes of nanoporous templates are used to synthesize, stabilize, and store nanoparticles. Crystalline nanoporous materials, which include MOFs, provide the entry point to particles spanning the micro- to low mesoscale (1–5 nm diameters). Block copolymers (BCP) are used to create mesoscale particles (2–30 nm). Importantly, these materials possess very low densities, minimizing the impact on the gravimetric storage capacity. This approach has significant advantages over previous template-based methods: monolithic pore dimensions; access to both micro- and mesoscale particles; and flexibility to modify the template organic component to create chemical or physical stabilization. Furthermore, ordered templates enable the use of the most sophisticated theoretical approaches, including highly accurate QMC methods, to guide materials development.

Results

Template Synthesis and Infiltration – MOF
templates having pore diameters ranging from ~ 1 –2 nm (e.g., Figure 1) and BCP templates with diameters ≥ 10 nm (e.g. Figure 2) were synthesized. MOFs were synthesized from published procedures. Porous BCP

FIGURE 1. Structure of Nanoporous Cubic Copper-Containing MOF Template

templates with pore diameters: ≥ 10 nm were synthesized from polystyrene and polymethylmethacrylate (PS-*b*-PMMA). Figure 2 shows a high-resolution scanning electron microscope (SEM) image of a nanoporous PS film obtained by selectively etching of PS-*b*-PMMA. Vertically oriented columns perpendicular to the substrate are sensitive to the surface preparation. To enable facile characterization of hydride uptake, we prepare these films on gold-coated quartz-crystal microbalance substrates for subsequent hydride infiltration. Other BCP templates are now being grown using spin coating and ultraviolet exposure to crosslink one polymer and degrade the other to create nanopores.

Solution-based infiltration methods for the binary hydrides LiH and MgH_2 were developed, using the organometallic precursors $\text{Mg}(\text{C}_4\text{H}_9)_2$ and $\text{CH}_3\text{CH}_2\text{Li}$ in organic solvents followed by thermal reduction to the corresponding hydrides. The complex hydrides NaAlH_4 , LiBH_4 and LiAlH_4 were infiltrated using hydride solutions in tetrahydrofuran. No template degradation is observed as a result of infiltration with these reactive compounds. Elemental analysis, infrared, and magic-angle spinning nuclear magnetic resonance methods (performed by Dr. Julie Herberg, LLNL) show that the hydride is present throughout the entire template. Loadings are relatively low (4 wt% in the case of NaAlH_4 , for example), but are more than sufficient to perform desorption experiments (see following).

FIGURE 2. SEM Image of Preliminary Nanoporous PS Film from the Selective Etching of PS-b-PMMA

Hydrogen Desorption Kinetics – The H_2 desorption kinetics of metal-hydride nanoparticles are very different from the corresponding bulk-phase materials (Figure 3). Using a unique Sandia instrument known as the simultaneous thermogravimetric modulated beam mass spectrometer (STMBMS), which provides mass data for evolved gas-phase species as a function of time under highly controlled temperature conditions, we obtained a detailed picture of the complex chemistry occurring during nanoparticle decomposition.

The desorption of H_2 by MOF-confined $NaAlH_4$ occurs at much lower temperatures than the bulk-phase material. STMBMS data for a series of temperature steps (Figure 3) reveals that complex desorption behavior by both bulk and MOF-confined $NaAlH_4$. Pure $NaAlH_4$ desorbs most of its H_2 (~70 wt%) at ~250°C (Figure 3A). H_2 from MOF-confined $NaAlH_4$ begins to desorb at 70°C, followed by a series of desorption events that culminate in steady-state release at 150°C (Figure 3B). Thus, the nanoscale hydride decomposes at temperatures $\geq 100^\circ\text{C}$ lower than bulk $NaAlH_4$. Simultaneous H_2 and solvent desorption at ~70°C also suggests that nanoscale effects may result from a combination of reduced size and the local chemical environment confining the clusters. These observations confirm the key hypothesis of this project, namely, that confinement within ordered nanoporous frameworks destabilizes metal hydrides.

Theoretical Modeling of Hydride Nanoparticles

– The group of Dr. Jeffery Grossman at University of California, Berkeley (UCB) completed computational modeling of Mg and $(MgH_2)_n$ clusters ($n = 1-40$) clusters, comparing QMC calculations with the results of DFT obtained from a variety of functionals and the literature (Figure 4). This computational benchmarking of popular computational methods reveals several important points. First, all methods indicate that the desorption energy decreases as the cluster size reaches very small

FIGURE 3. A. Amount of H_2 Released from $NaAlH_4$ -Infiltrated MOF Compared with Pure $NaAlH_4$. B. Rate of H_2 Released from $NaAlH_4$ @ Cu_3BTC_2 MOF Compared with Neat $NaAlH_4$

FIGURE 4. Comparison of H_2 Desorption Energies for $(MgH_2)_n$ Clusters Predicted by QMC vs. Various DFT Functionals

dimensions. However, there is enormous variation in the *quantitative* trends. For example, the results of Wagemans et al. [1] predict that the desorption energy drops below the bulk value at $n = 12$, while QMC predicts that the desorption energy is actually *higher* than the bulk value at this size. Differences between DFT and QMC at this size are as high as 25 kJ/mol. We are confident of the accuracy of QMC, based on excellent agreement with the bulk value and the overall convergence behavior of the code. These results suggest that size may not be the only factor at work, since

various investigators report accelerated kinetics for both MgH_2 and NaAlH_4 at sizes considerably larger than this (≥ 2 nm for NaAlH_4 supported on carbon nanofibers and ~ 5 nm for MgH_2 colloids).

Extension of the NanoPEGS Model to Nanoclusters – The Prototype Electrostatic Ground State (PEGS) code, a highly successful model that identifies the correct ground-state structure for charged materials, was extended to nanoscale clusters by its developer, Prof. Eric Mazjoub. NanoPEGS was first applied to MgH_2 clusters and provided prototype structures for DFT and quantum-chemistry calculations performed at UCB. Nano-PEGS clusters of NaAlH_4 , $\text{Ca}(\text{BH}_4)_2$, and $\text{Mg}(\text{BH}_4)_2$ are currently being explored. The results show that electrostatics are a useful simplification of the interatomic potential in the ionic as well as complex hydrides, allowing a rapid investigation of cluster geometries for nanoscale as well as bulk materials.

Conclusions and Future Directions

- MOFs are well-defined, chemically stable templates for metal-hydride nanoparticles.
- Hydride confinement shifts H_2 desorption to lower temperatures, but both the size and chemical environment of the templates pores.
- H_2 desorption energies predicted by DFT methods may contain significant nonsystematic errors and should be checked against high-level methods to assess their accuracy.
- Next year we will systematically vary both pore dimensions and chemical environment to identify the factors controlling nanoscale hydride stability, and develop synthetic methods to enable compositional tuning of hydride properties. Computational modeling using QMC, DFT, and NanoPEGS will continue to guide synthetic efforts. We also will down-select to specific hydrides and optimize the infiltration methods to maximize loading.

FY 2009 Publications/Presentations

1. R.K. Bhakta, J.L. Herberg, B. Jacobs, A. Highley, R. Behrens, Jr., M.D. Allendorf “Metal organic frameworks as templates for nanoscale NaAlH_4 ,” communication submitted to *J. Amer. Chem. Soc.*, May 2009.
2. Z. Wu, M.D. Allendorf, J.C. Grossman “Nanoscale effects on metal hydride thermodynamics: quantum Monte Carlo benchmarking of density functional theory,” communication submitted to *J. Amer. Chem. Soc.*, July 2009.
3. R.K. Bhakta, J.L. Herberg, R. Behrens, and M.D. Allendorf “Metal-organic frameworks as templates for nanoscale metal hydrides,” Spring meeting, American Chemical Society, Salt Lake City, March 22–26, 2009.
4. M. D. Allendorf, Tech Team briefing, Sept. 12, 2008, Livermore, CA.
5. M.D. Allendorf, Metal Hydride Center of Excellence Face-to-face meeting, Dec. 19, 2008.
6. E.H. Majzoub “A computational tool for complex ionic hydrides: global optimization using prototype electrostatic ground states,” invited presentation, Purdue Hydrogen Symposium 2009, Purdue University, Lafayette, Indiana, 22 April, 2009.
7. E.H. Majzoub “Computational approach to the structure and thermodynamics of metal borohydrides,” American Physical Society March Meeting, March 2009.
8. E.H. Majzoub “Prototype electrostatic ground state approach to predicting crystal structures of ionic compounds: Applications to hydrogen storage materials,” Hydride Materials Theory Workshop, Materials Research Society Meeting, San Francisco, California, 24 March, 2008.

References

1. Wagemans et al. (2005)

IV.A.4 Discovery of Novel Complex Metal Hydrides for Hydrogen Storage through Molecular Modeling and Combinatorial Methods

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Project Start Date: May 1, 2004
Project End Date: June 30, 2009

- (E) Charging/Discharging Rates
- (P) Lack of Understanding of Hydrogen Physisorption and Chemisorption

Technical Targets

This project uses virtual high-throughput screening by computer modeling and combinatorial experimentation to identify promising metal hydrides for vehicular on-board hydrogen storage applications meeting DOE 2010 system targets:

- Useable, specific-energy from H₂: 2 kWh/kg
- Useable energy density from H₂: 1.5 kWh/L
- Storage system cost: \$4/kWh net
- Cycle life: 1,000 cycles
- Minimum and maximum delivery temperature: -40/85°C
- System fill time: 3 minutes for a 5-kg hydrogen system.

TABLE 1. UOP Progress toward Meeting DOE On-Board Hydrogen Storage Targets (Data is based on material only, not system)

Storage Parameter	Units	2010 Target	LiBH ₄ -LiNH ₂ -MgH ₂
Specific Energy	kWh/kg	2.0	1.1
Energy Density	kWh/L	1.5	0.8

Objectives

Discovery of complex metal hydrides through molecular modeling and combinatorial methods which will enable a hydrogen storage system that meets DOE 2010 performance goals. The deliverables include:

- Optimized material
- Accompanying documentation

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) System Weight and Volume
- (B) System Cost
- (D) Durability/Operability

Accomplishments

The entire year was spent trying to get the High Throughput Synthesis System operational. A critical piece of the system, a powder doser, had not operated properly. The piece was redesigned several times by the vendor, but ultimately it could not carry out the tasks it was designed for. Since we are now two years past the original closing date of this project and there is no progress making the High Throughput Synthesis System functional, a decision was made to shut down the project as of June 30, 2009.

Introduction

Metal hydrides have the potential for reversible on-board hydrogen storage with hydrogen release at low temperatures and pressures. However, known hydrides are either too heavy (such as LaNi₅H₆), or require high

temperature to release hydrogen (such as MgH_2). This project will systematically survey complex hydrides to discover a material which would enable a hydrogen storage system that meets DOE's 2010 goals.

Approach

The team is applying combinatorial experimentation and molecular modeling to discover materials with optimum thermodynamics and kinetics for on-board hydrogen storage. Virtual high-throughput screening exploits the capability of molecular modeling to estimate the thermodynamics on the computer more quickly than can be measured in the laboratory. First-principles calculations are being used to predict thermodynamic properties of these new materials. Even more importantly, the coupling of combinatorial experiments with molecular modeling of structural and thermodynamic properties is providing insights into the underlying mechanisms of action in these complex materials, permitting the design of hydrogen storage materials which would never have been envisioned otherwise.

Results

The High Throughput Synthesis System has proven problematic in regard to the controlled transfer of finely ground powders. The small scale of the combinatorial experiments requires fraction of a milligram accuracy of the powder dosing component of the High Throughput Synthesis System. This last year we have gone through several iterations with the vendor to develop a tool that can function accurately and reproducibly without any upsets. Several new incarnations of the powder dosing tool is looked promising, but to date, none have operated reliably. Hence, after a two year extension, the project has now been shut down.

Conclusions and Future Directions

The project is now concluded, since we have failed to make the High Throughput Synthesis System operational. Our work over the course of this project included a high throughput assay to evaluate hydrogen storage capacities, but the synthesis was carried out one sample at a time with some parallel steps. For the extended portion of the project, we tried to use the high throughput synthesis in concert with the high throughput assay. Unfortunately we never overcome the hurdle presented by our powder dosing tool. As of June 30, 2009, the project is ended.

IV.A.5 Center for Hydrogen Storage Research at Delaware State University*

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Start Date: July 1, 2006

Projected End Date: June 30, 2009

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Technical Targets

This project is conducting fundamental studies of complex borohydride materials. Insights gained from these studies will be applied toward the design and synthesis of hydrogen storage materials that meet DOE's 2010 goal of 6 wt% hydrogen storage for the system. Table 1 summarizes the targets.

TABLE 1. Targets

Storage Parameter	Units	Target
System Gravimetric Capacity: Usable, specific-energy from H ₂ (net useful energy/max system mass)	kW-h/kg	1.5
System Volumetric Capacity: Usable energy density from H ₂ (net useful energy/max system volume)	kW-h/L	1.2
Storage System Cost (and fuel cost)	\$/kWh	6

Accomplishments

This project is conducting measurements on complex hydrogen storage systems to determine if they will meet DOE's targets for hydrogen storage.

- Have further characterized the LiBH₄/CaH₂ system. Cycling studies done at 450°C indicate that the absorption capacity decreases from 9 wt% hydrogen to less than 3 percent after 25 cycles.
- Have completed the analyses on a double cation borohydride system using thermal gravimetric analysis (TGA), thermally programmed desorption (TPD) and pressure-composition isotherm (PCI) analyses. The hydrogen sorption characteristics of systems of general composition MM'_{m-n}(BH₄)_m (M= Cu, Mn and Zr, M'= Li or Na) were studied. The Mn-containing material was found to release hydrogen at about 130°C but there was also some evidence of diborane release as well. These materials were stable solids under the conditions used.
- Have done kinetics studies on the MgH₂/LiBH₄ system, with varying amounts of LiBH₄, to determine desorption rates using constant pressure driving forces. The rates were found to decrease with increasing amounts of LiBH₄ in the system.

Objectives

- Identify complex hydrides that have the potential to meet DOE's goals for storage and demonstrate the optimum temperature and pressure ranges under a variety of conditions.
- Improve the sorption properties of systems that have been identified as good prospects for hydrogen storage.
- Determine the cyclic stability of new materials and develop strategies for improving reversibility.
- Perform kinetic modeling studies and develop methods for improving kinetics and lowering reaction temperatures, thereby reducing refueling time.
- Extend the studies to include other complex hydrides, that have greater hydrogen storage potential.

Technical Barriers

This project addresses the following technical barriers taken from the Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) System Weight and Volume
- (D) Durability/Operability
- (E) Charging/Discharging Rates

Introduction

Developing a safe, cost-effective, and practical means of hydrogen storage is essential for the advancement of hydrogen and fuel cell technologies. Materials such as sodium alanate were a vast improvement in storage capacity over most traditional hydrides. However, even the alanates fall short of meeting DOE's long-term hydrogen storage goals. Therefore interest has now focused on destabilized hydrides which have even greater potential for hydrogen storage.

The main goals of this project are (1) Establish a Center for Hydrogen Storage Research at Delaware State University for the preparation and characterization of selected complex metal hydrides and the determination their suitability for hydrogen storage. (2) Develop methods for the synthesis, characterization, and modeling of complex hydrides using $\text{LiBH}_4/\text{MgH}_2$ as a model system. (3) Identify the most promising types of complex hydrides destabilized hydrides and demonstrate the optimum temperature/pressure range and sorption kinetics of the hydrides under a variety of conditions. (4) Determine their cyclic stability and develop improved sorption catalysts. Extend the studies to include other complex hydrides that have greater hydrogen storage potential than the destabilized hydrides such as ternary borohydride systems. (5) Perform kinetic modeling studies and develop methods for improving kinetics and lowering reaction temperatures.

Approach

To achieve the project objectives, new materials are being developed and characterized using a variety of techniques. Sample preparations prior to analysis were done in an argon-filled glove box (Vacuum Atmosphere Company). The hydrides were made by first ball milling the raw materials in a SPEX 8000 Mixer Miller and then directly combining them with hydrogen in a Sieverts apparatus. X-ray powder diffraction in a Panalytical X'pert Pro MPD Analytical X-Ray Diffractometer was used to confirm the formation of product and to determine phase purity.

TGA and TPD were used to determine the thermal stability and the hydrogen capacity of the mixtures. The TGAs were done in a Lab System-Diamond thermogravimetric/differential thermal analysis. This instrument was placed inside of an argon-filled glove box so that samples can be analyzed with virtually no exposure to air and moisture. The TPD analyses were carried out in a PCI unit. The instrument was supplied by Advanced Materials Corporation. Kinetic measurements were done to determine the overall reaction rates. Cycling measurements were done to determine the stability of the materials when subjected to repeated hydrogenation and dehydrogenation cycles. The B-H bond strength of the various synthesized double-cation borohydrides

were compared via Shimadzu Infrared Prestige-21 FTIR spectrophotometer. This instrument operates in a single-beam mode and is capable of data collection over a wave number range of $7,800\text{ cm}^{-1} \sim 350\text{ cm}^{-1}$. Residual gas analyses (RGA) were done in a RGA Pro 2000. The instrument was produced by Stanford Research Systems and distributed by Hy-Energy LLC in Newark, CA.

Results

In the previous year, the main focus of the research was the analyses of $\text{CaH}_2/\text{LiBH}_4$ mixtures. In those studies, the mixtures were found to reversibly absorb and release 9 wt% hydrogen. In the past year we did cycling studies to determine the stability of the materials when subjected to repeated hydrogenation and dehydrogenation cycles. Cycling studies done at 450°C indicate that the absorption capacity decreases from 9 wt% hydrogen to less than 3 wt% after 25 cycles. In addition, the $\text{CaH}_2/\text{LiBH}_4$ system absorbs and releases hydrogen at temperatures in the 400°C range, which is too high for fuel cell applications. Therefore an effort was made to develop other borohydride systems that had lower operating temperatures. One such system was the $\text{MM}'_{m-n}(\text{BH}_4)_m$ system ($\text{M} = \text{Cu}, \text{Mn}$ and Zr , $\text{M}' = \text{Li}$ or Na). The materials in this system were prepared by mechanically milling mixtures of $\text{CuCl}_2 + 3\text{LiBH}_4$, $\text{MnCl}_2 + 3\text{LiBH}_4$, and $\text{ZrCl}_4 + 6\text{LiBH}_4$.

Figure 1 shows the powder X-ray diffraction (XRD) profiles of the complex mixtures mechanically milled for 10 hours. The diffraction peaks measured at angles 30, 35, 50, 60 and 63 degrees are identified as LiCl , although slight peak shifts were observed, probably due to the partial substitution of M for Li in LiCl . There are no major diffraction peaks of the starting materials of MnCl_2 and LiBH_4 in the spectrum of $\text{MnLi}(\text{BH}_4)_3$, indicating that the reaction has progressed to completion. On the other hand, the diffraction peak of one of the starting material (LiBH_4) was present in the spectra of $\text{CuLi}(\text{BH}_4)_3$ and $\text{ZrLi}_2(\text{BH}_4)_6$ at angle 44

FIGURE 1. XRD spectra for the $\text{MLi}'_{m-n}(\text{BH}_4)_m$ system ($\text{M} = \text{Cu}, \text{Mn}$ and Zr). There are no X-ray diffraction peaks of $\text{MM}'_{m-n}(\text{BH}_4)_m$ in the profiles of the samples due possibly to the absence of long range order in the structure of the synthesized samples.

degree. This indicates that the reaction did not proceed to completion under the milling conditions in this experiment. The formation of NaCl is an indication that complex borohydrides were formed. There are no XRD peaks of $MM'_{m-n}(BH_4)_m$ in the profiles of the samples prepared by mechanical ball milling, this might be due to the absence of long range order in the structure of the synthesized samples.

Fourier transform infrared spectroscopy (FTIR) was used to determine if the boron–hydrogen bonds had been affected by the presence of the cations (Cu, Mn or Zr). Figure 2 shows the composite FTIR spectrum of the synthesized double-cation borohydrides. For $M\text{Li}(\text{BH}_4)_n$ ($M=\text{Cu}$, Mn and Zr) complexes synthesized earlier, various peaks were observed from the infrared spectra. All of the spectra display similar characteristics. However, in the region of $1,400\text{--}1,200\text{ cm}^{-1}$, one of these materials display a significant difference from the others. The FTIR spectrum of all the materials except $\text{MnLi}(\text{BH}_4)_3$ have a single peak in this region. This indicates that the $\text{MnLi}(\text{BH}_4)_3$ material might have a different desorption behavior than the others.

TPD was used to determine the thermal stability and the hydrogen capacity of the mixtures. The composite TPD of the borohydride complexes prepared is shown in Figure 3. It can be seen that the partial substitution of Cu, Mn and Zr in LiBH_4 truly lowers the desorption temperature when compared with the desorption temperature of LiBH_4 . The $\text{MnLi}(\text{BH}_4)_3$ complex appears to be the best of the group. The Mn-containing material was found to release hydrogen at about 130°C . This is a big improvement over the 400°C temperature observed for the $\text{CaH}_2/\text{LiBH}_4$ system. However, when RGAs were done the presence of diborane was observed in all the synthesized complex borohydrides except $\text{CuLi}(\text{BH}_4)_3$. The loss of diborane from the complex borohydrides destroys the reversibility of the complex borohydrides.

FIGURE 2. FTIR spectra of LiBH_4 , $\text{CuLi}(\text{BH}_4)_3$, $\text{MnLi}(\text{BH}_4)_3$ and $\text{ZrLi}_2(\text{BH}_4)_6$. The spectra are all similar but the Mn-containing complex displays two peaks in the $1,200\text{--}1,400\text{ cm}^{-1}$ region that are absent in the others.

A kinetics study was also done on the $\text{MgH}_2/\text{LiBH}_4$ system, with varying amounts of LiBH_4 , to determine the effect of LiBH_4 content on the desorption rates. The ratios of LiBH_4 to MgH_2 used in these studies were 2, 4 and 7. It was found that when the ratio of the plateau pressure/applied hydrogen pressure (N-value) was kept constant, the reaction rates decreased as the amount of LiBH_4 increased. The N-value is directly proportional to the thermodynamic driving force. As an example of these studies, the rate curves for the desorption kinetics at 450°C and $N = 3, 4$, and 5 are shown in Figure 4. It was found that when the N-value was increased, the reaction rates increased. This demonstrates the importance of keeping the N-value constant when comparing reaction kinetics of different materials.

FIGURE 3. TPD of double-cation borohydrides. The desorption of gases by $\text{MnLi}(\text{BH}_4)_3$ starts around 116°C . $\text{CuLi}(\text{BH}_4)_3$ starts around 199°C , and $\text{ZrLi}_2(\text{BH}_4)_6$ starts around 81°C .

FIGURE 4. Desorption kinetics of the $\text{MgH}_2/\text{LiBH}_4$ system at 450°C and $N = 3, 4$, and 5 . The N-value is defined as the ratio of the dissociation plateau pressure to the applied hydrogen pressure.

Conclusions and Future Directions

- Cycling studies done at 450°C on the $\text{LiBH}_4/\text{CaH}_2$ system indicate that the absorption capacity decreases from 9 wt% hydrogen to less than 3 wt% after 25 cycles. Thus, this material is not suitable for hydrogen storage applications in its present form.
- Analyses on double cation borohydride systems of general composition $\text{MM}'_{m-n}(\text{BH}_4)_m$ ($\text{M} = \text{Cu, Mn}$ and Zr , $\text{M}' = \text{Li}$ or Na) show that the Mn-containing material begins to release hydrogen at about 130°C. This temperature is low enough for fuel cell applications. However, the release of diborane leads to irreversibility and thus a way to eliminate this need to be found.
- Kinetics studies were done on the $\text{MgH}_2/\text{LiBH}_4$ system, with varying amounts of LiBH_4 , to determine desorption rates using constant pressure driving forces show that the rates decrease with increasing amounts of LiBH_4 in the system. Thus, it is desirable to find complex systems with more metal and less complex anion.

In the next fiscal year we propose to perform hydrogen storage studies on some new destabilized complex hydrides that have been predicted by first principles calculations to be suitable hydrogen storage materials. We will develop methods for the synthesis, characterization, and modeling of these new complex hydrides as well as developing new catalysts and engineering techniques for increasing reaction rates and lowering reaction temperatures. Nanotechnology will be used to reduce or eliminate the release of any diborane.

FY 2009 Publications/Presentations

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2. H. Yang, A. Ojo, P. Ogaro and A.J. Goudy, "Hydriding and Dehydriding Kinetics of Sodium Alanate at Constant Pressure Driving Forces" *J. Phys Chem.*, (2009) In press.
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IV.A.6 Effects and Mechanisms of Mechanical Activation on Hydrogen Sorption/Desorption of Nanoscale Lithium Nitrides and Lithium Borohydrides

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Subcontractors:
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Objectives

- Investigate the effects and mechanisms of mechanical activation on hydrogen sorption/desorption behavior of Li_3N - and LiBH_4 -based materials.
- Develop a novel, mechanically activated, nanoscale Li_3N - or LiBH_4 -based material that is able to store and release ~10 wt% hydrogen at temperatures below 100°C with a plateau hydrogen pressure of less than 10 bar.

Technical Barriers

This project addresses the following technical barriers from the Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) System Weight and Volume
- (E) Charging/Discharging Rates

Technical Targets

This project is to develop a fundamental understanding of effects and mechanisms of mechanical activation on hydrogen storage capacity and sorption/desorption kinetics of nanoscale Li_3N - and LiBH_4 -based materials. Insights gained from these studies will be applied to producing a novel, mechanically activated, nanoscale Li_3N - or LiBH_4 -based material that meets the following DOE 2010 hydrogen storage targets:

- Cost: \$4/kWh net
- System gravimetric capacity: 1.5 kWh/kg
- System volumetric capacity: 0.9 kWh/L
- Charging/discharging rates: 4.2 min for 5 kg

Progress towards meeting the DOE on-board hydrogen storage targets made up to Fiscal Year 2009 is summarized in Table 1.

TABLE 1. Progress Towards Meeting the DOE On-Board Hydrogen Storage Targets

Storage Parameter	Units	2010 System Target	FY09 Material Status
Specific Energy	kWh/kg (kg H_2 /kg system)	1.5 (0.045)	3.17 at 265°C (0.095 at 265°C)
Energy Density	kWh/L (kg H_2 /L system)	0.9 (0.028)	2.54 at 265°C (0.079 at 265°C)
Charging/ Discharging Rate (system fill time for 5 kg)	min	4.2	300 at 265°C

Accomplishments

- Developed a two-step ball milling procedure to improve the solid-state hydriding and dehydriding kinetics of $\text{LiBH}_4 + \text{MgH}_2$ systems.
- Demonstrated the solid-state hydriding and dehydriding of $\text{LiBH}_4 + \text{MgH}_2$ systems with 9.5 wt% hydrogen uptake and 4.5 wt% hydrogen release at 265°C. These are the best hydriding and dehydriding properties for the $\text{LiBH}_4 + \text{MgH}_2$ system ever reported in the open literature.
- Identified the solid-state hydriding mechanism of the $\text{LiBH}_4 + \text{MgH}_2$ system and established a partial ion-exchange model to guide the improvement of the diffusion-controlled hydriding reaction.
- Achieved the hydrogen release from nanoscale LiBH_4 confined within carbon aerogels (CAs) at temperatures as low as 80°C with the peak

releasing temperature at 165°C and the completion temperature at 275°C. These H₂ release temperatures are the lowest ever reported in the open literature for LiBH₄. More importantly, these hydrogen release behaviors approach the DOE target – releasing H₂ below 100°C!

- Demonstrated that the hydrogen released from CA-confined LiBH₄ contained no borane – an impurity that is likely to poison proton exchange membrane (PEM) fuel cells.

Introduction

A key component for the hydrogen economy is fuel cell vehicles which, in turn, depend critically upon advanced hydrogen storage materials. The challenge is to develop a storage material that simultaneously satisfies three competitive requirements: (i) high hydrogen density, (ii) reversibility of hydrogen release/uptake cycle near the ambient temperature and pressure, and (iii) fast release/uptake kinetics. This project is aimed at investigation and development of such hydrogen storage materials with capabilities to reversibly uptake and release hydrogen near the ambient temperature and pressure.

Approach

To achieve the project objectives, we have employed nano-engineering and mechanical activation approaches to develop hydrogen storage materials that simultaneously satisfy the three requirements mentioned above. In the last year, we switched our focus from (LiNH₂+LiH)-based systems to (LiBH₄+MgH₂)-based systems because the latter have a theoretical storage capacity of 11.5 wt% H₂, while the former only have a theoretical storage capacity of 6.5 wt% H₂. It was shown previously that hydriding and dehydriding processes of both systems were diffusion controlled [1,2]. Therefore, nano-engineering and mechanical activation approaches are pursued to reduce the hydride particle sizes, increase their surface areas, and mix the reactants at the nanoscale – all of which will enable rapid sorption and desorption of hydrogen molecules on the solid surface, provide large interfacial area for reactions between solid hydrides, and reduce the diffusion distance of hydrogen within the solids.

Results

Figure 1 shows the hydriding performance of a 2LiH+MgB₂ mixture processed with a two-step ball milling procedure. Note that this two-step ball milled mixture exhibits hydrogen uptake of 9.5 wt% at 265°C. This is the best hydriding property at 265°C ever

FIGURE 1. Hydrogenation behavior of a two-step ball milled 2LiH + MgB₂ mixture. The two-step ball milling entails (a) ball milling at room temperature for 120 h and then (b) ball milling at liquid nitrogen temperature for 1 h with the addition of 15 vol% graphite. The hydrogenation was conducted under a hydrogen pressure of 90 bar with the heating condition indicated.

reported in the open literature for LiBH₄+MgH₂ systems. The overall reaction corresponding to the hydriding reaction of the 2LiH+MgB₂ mixture is [3]

The superior hydriding performance shown in Figure 1 results from the two-step ball milling procedure which entails ball milling the 2LiH+MgB₂ mixture at room temperature for 120 h and then at liquid nitrogen temperature for 1 h with addition of 15 vol% graphite at the second-step milling. The first-step ball milling reduces the grain sizes of LiH and MgB₂ to 7.5 and 6.8 nm, respectively, and mixes them uniformly within nanostructured particles with the average size of 260 nm [2]. This ball milled mixture can uptake 8.3 wt% H₂ at 265°C because of the enhanced diffusion coefficients due to the presence of large grain boundary and interfacial areas within the nanostructured particles [2]. The second-step ball milling, although in a relatively short duration, introduces nano-graphite to the grain boundaries and interfaces within nanostructured particles because of frequent fracture and cold welding of particles during ball milling. The presence of the trapped nano-graphite leads to more open structures at the grain boundaries and interfaces, thereby increasing the diffusion rates of H, Mg, Li and B all of which are needed for the hydriding reaction. It should be pointed out that two-step ball milling is necessary to achieve this superior performance because long-time ball milling with the addition of graphite results in reactions between LiH and graphite during ball milling and degrades the hydriding performance rather than improving it (not shown here).

The two-step ball milling procedure also improves the dehydriding properties. As shown in Figure 2, the one-step ball milled mixture can only release 2.0 wt% H₂ at 265°C, whereas the two-step ball milled counterpart

FIGURE 2. A comparison of the dehydrogenation behavior between a two-step ball milled $2\text{LiH} + \text{MgB}_2$ mixture (i.e., 120+1 h sample) and a one-step ball milled mixture (120 h sample). Both ball milled samples were first hydrogenated under the condition shown in Figure 1. After the hydrogenation, the dehydrogenation was conducted under an evacuated condition (~ 0.03 bar) with the heating condition indicated.

can release 4.5 wt% H_2 , exhibiting a 125% improvement over the one-step ball milled mixture. The improvement is attributed to the presence of the trapped nano-graphite within nanostructured particles. Note that releasing 4.5 wt% H_2 requires the participation of a large amount of LiBH_4 and all of MgH_2 in the dehydriding process. It has been shown previously that LiBH_4 and MgH_2 do not react directly in the dehydriding process [2-6]. Instead, MgH_2 decomposes into Mg and H_2 first and then the newly formed Mg and H_2 react with LiBH_4 to produce LiH , MgB_2 and H_2 . It is proposed that the trapped nano-graphite in the two-step ball milled mixture enhances the diffusion rate of Mg at grain boundaries and interfaces, thereby accelerating the reaction among Mg , LiBH_4 and H_2 to produce LiH , MgB_2 and H_2 with higher rates.

Figure 3 shows a model of the molecular interaction between LiH and MgB_2 during long-time ball milling. This model is proposed based on the detailed nuclear magnetic resonance (NMR) analysis [7]. Before ball milling, all the magnesium atoms are located between the boron layers and each is along the central symmetric axis of the boron hexagonal structure (Figure 3a). After long-time ball milling, a significant amount of magnesium sites are exchanged with lithium (Figure 3b) to form a compound with a composition of $(\text{Mg}_{1-x}\text{Li}_{2x})\text{B}_2$ to maintain the charge balance. Each expelled magnesium combines with two protons from LiH to form MgH_2 . The formed MgH_2 is located at the immediate surface of the $(\text{Mg}_{1-x}\text{Li}_{2x})\text{B}_2$ structure and in an amorphous state. This partial ion exchange mechanism can be described by

FIGURE 3. Proposed structure changes of the $\text{LiH} + \text{MgB}_2$ mixture: (a) before and (b) after long-time ball milling.

where x is a variable changing from 0 (for MgB_2) to less than 1, depending on the time of ball milling. The model proposed is consistent with the NMR analysis [7], showing that approximately 50% of MgB_2 has been converted to MgH_2 accompanied by only $\sim 1\%$ LiBH_4 formation after ball milling at room temperature for 120 h. The model proposed is also consistent with the previous X-ray diffraction (XRD) analysis [2], showing the absence of MgH_2 after 120 h ball milling because of the amorphous state of MgH_2 . This model is also in good accordance with the Fourier transform infrared analysis, showing little LiBH_4 formation [7]. The formation of the compound $(\text{Mg}_{1-x}\text{Li}_{2x})\text{B}_2$ is likely the key reason for the observed enhancement in the subsequent solid-state hydrogenation [2]. Although the detail of hydrogenation mechanism remains to be studied, one possible reaction pathway is the continued Mg - Li ion exchange within $(\text{Mg}_{1-x}\text{Li}_{2x})\text{B}_2$ and simultaneous hydrogenation of $(\text{Mg}_{1-x}\text{Li}_{2x})\text{B}_2$. It is noted that the extreme case of the continued Mg - Li ion exchange is the formation of the LiB crystal. LiB has been observed experimentally [8]. Furthermore, the first-principles calculations reveal that Li is in the state of Li^+ ion in LiB [9] and stabilizes the hexagonal layers of boron in LiB [10]. Therefore, gradual transition from MgB_2 to LiB through the intermediate $(\text{Mg}_{1-x}\text{Li}_{2x})\text{B}_2$ will involve no change in the hexagonal layers of boron and no charge unbalance. Although pure LiB may not form during the subsequent hydrogenation because of the simultaneous Mg - Li ion exchange and hydrogenation of $(\text{Mg}_{1-x}\text{Li}_{2x})\text{B}_2$, the formation of Li -rich $(\text{Mg}_{1-x}\text{Li}_{2x})\text{B}_2$ compound is expected to facilitate the formation of LiBH_4 because the removal of Mg from MgB_2 is necessary for the formation of LiBH_4 .

Figure 4 shows the H_2 gas profile from nanoscale LiBH_4 confined within CAs during a thermogravimetric analysis (TGA). It reveals that CA-confined LiBH_4 can release H_2 at temperatures as low as 80°C with the peak releasing temperature at 165°C and the completion temperature at 275°C . These H_2 release temperatures are the lowest ever reported in the open literature for

FIGURE 4. The temperature profile during a thermogravimetric (TG) analysis of LiBH_4 confined within a CA and the corresponding effluent hydrogen profile measured using an on-line mass spectrometer. The heating condition was: (i) held at room temperature for 60 min, (ii) jumped to 80°C and held for 300 min, and (iii) heated at 2°C/min to 550°C. All the procedures were conducted in an argon-filled glovebox with flowing argon in the TG chamber.

LiBH_4 . More importantly, this dehydriding property approaches the DOE target – releasing H_2 below 100°C! Furthermore, no emission of borane, B_2H_6 – an impurity that is likely to poison PEM fuel cells and frequently found in the hydrogen released from LiBH_4 [11], is detected in the entire temperature range (not shown in Figure 4), suggesting that emission of borane can be avoided if hydrogen is released at low temperatures. We believe that the unprecedented enhancement in the dehydriding behavior of LiBH_4 shown in Figure 4 is due to the formation of sub-nm particles, which results in a drastically reduced diffusion distance and the associated improvement in the thermodynamic properties. By characterizing CAs before and after infiltration of LiBH_4 in a tetrahydrofuran (THF) solution and removing of the THF solvent under vacuum at room temperature for 20 h, we find that the average diameter of the CA-confined LiBH_4 particles is ~0.75 nm. It is these sub-nm particles that lead to the unprecedented enhancement in the dehydriding behavior of LiBH_4 . It should be pointed out that to ensure that the H_2 gas observed in Figure 4 is from LiBH_4 only, we have conducted the identical TGA experiments coupled with an on-line mass spectrometer on the CA alone, THF solvent only, and THF-infiltrated CAs. The results indicate that hydrogen is from LiBH_4 only.

Conclusions and Future Directions

The successful demonstration of 9.5 wt% hydrogen uptake and 4.5 wt% hydrogen release of $\text{LiBH}_4 + \text{MgH}_2$ systems in the solid state without any catalysts indicates that nano-engineering and mechanical activation are

effective methods in enhancing diffusion-controlled reactions. Therefore, in the remainder of FY 2009, efforts will be focused on exploring the integration of nano-engineering, mechanical activation, and addition of effective transition metals to further increase the diffusion rates and thus reduce the hydrogen uptake and release temperature of $\text{LiBH}_4 + \text{MgH}_2$ systems.

The unprecedented enhancement in the dehydriding behavior of nanoscale LiBH_4 confined within CAs is scientifically and technologically important. Thus, its hydriding and dehydriding reversibility will be investigated in the remainder of FY 2009. Furthermore, the storage capacity of CA-confined LiBH_4 will be increased through high loading of LiBH_4 in CAs and the relationship between the LiBH_4 loading and the kinetics of hydriding and dehydriding processes will be studied in order to provide guidelines for developing high-performance hydrogen storage materials that meet the DOE 2015 targets.

FY 2009 Publications/Presentations

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IV.B.1a 2009 Overview - DOE Chemical Hydrogen Storage Center of Excellence (CHSCoE)

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Start Date: March 1, 2005

Projected End Date: September 30, 2010

Objectives of the Center

- Implement a coordinated approach to identify, research, develop, and validate advanced on-board chemical hydrogen storage systems to overcome technical barriers and meet DOE Hydrogen Storage 2010 system goals.
- Design, synthesize, and test materials and compositions to control the thermochemistry and kinetics of hydrogen release.
- Develop energy and chemically efficient off-board spent fuel regeneration for the complete fuel cycle.
- Assess concepts and systems for hydrogen release and spent fuel regeneration using supporting engineering analysis and validation to rank viable candidates.
- Down select most promising chemical systems for more detailed materials and engineering development.
- Develop most promising chemical hydrogen storage materials with potential to meet 2010 targets.
- Perform lab-scale engineering studies to evaluate performance of hydrogen storage systems.
- Develop life cycle analysis.
- Transfer chemical hydrogen storage systems information to Hydrogen Storage Engineering Center of Excellence, and receive feedback from its analyses.

Technical Barriers

This project addresses the following technical barriers from the Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-

Year Research, Development and Demonstration Plan (MYRDDP):

- (A) System Weight and Volume
- (B) System Cost
- (C) Efficiency
- (D) Durability/Operability
- (E) Charging/Discharging Rates
- (J) Thermal Management
- (K) System Life-Cycle Assessments
- (R) Regeneration Processes
- (S) By-Product/Spent Material Removal

Technical Targets

While all of the relevant targets detailed in the DOE MYRDDP will be addressed, the Center's main emphasis focuses on the material and efficiency requirements for storage of hydrogen in chemical bonds. The Center has developed interim technical guidelines to facilitate down-selection of promising materials for further development. The Center's key criteria for down-selection of storage materials include gravimetric and volumetric hydrogen capacities, as well as hydrogen release rate and temperature. Gravimetric capacity of materials must exceed 7 wt%, with the potential to exceed 9 wt%. The goal for temperature is for hydrogen release to occur with high rate below 100°C, with an interim goal of release occurring at high rates below 200°C. The Center's criterion for the rate of hydrogen release, 0.02 g H₂/s/kW, is the DOE 2010 target. A tabulation of all of the Center's interim targets is published in the Center's 2008 annual report, http://www.hydrogen.energy.gov/annual_progress08_storage.html#b.

The targets for regeneration of spent fuel include an interim target of 40% energy efficiency, with an ultimate goal of 60% energy efficiency, with chemical efficiencies approaching 100%, e.g. minimum losses to byproducts.

Accomplishments

Accomplishments from across the Center are organized into four main areas: 1). Hydrogen Release, 2). Spent Fuel Regeneration, 3). New Materials, and 4). Engineering Supporting R&D. The 2009 highlights from each of these areas are outlined below.

- Hydrogen Release from Ammonia Borane (AB):
 - Mitigation of foaming well demonstrated for solid AB with scaffold, nano BN, methylcellulose.

- Demonstrated ionic liquid/AB mixtures release hydrogen up to 10% wt% H₂ at temperatures less than 110°C.
- Demonstrated high rates at T as low as 70°C with non-precious group metal heterogeneous catalysts demonstrated.
- Identified liquid fuels of alkylamine borane/AB mixtures.
- Identification of impurities, mechanism of origin, and quantification studies underway for all pathways being actively pursued.
- Spent Fuel Regeneration, First Fill Processes, and Boron Resources Studies:
 - Demonstrated regeneration of AB from spent fuel.
 - Cost analysis of first fill AB synthesis completed for leading process candidates.
 - Identified additional promising first fill processes based upon direct digestion and reduction of spent fuel with hydrazine that may improve both cost and efficiency.
 - Added new partner, US Borax. Their work is to provide updated boron minerals reserves estimates that indicate U.S. supply of B is adequate to meet B-fuel requirements of DOE hydrogen vehicle market penetration scenarios.
- New Materials Development:
 - Li amidoborane demonstrated to have very high activation energy of release that is beneficial to onboard shelf life considerations.
 - Developed an ammonium borohydride synthesis that results in materials with vastly improved thermal stability, and has potential as a ‘first fill’ source of pure AB.
 - K, Mg, Ca-amidoboranes synthesized, hydrogen release characterized, and structures determined which assists our understanding of hydrogen release from these metal substituted AB derivatives.
 - Added new partner, University of Oregon. Synthesized a number of new cyclo-CBN compounds that are potentially onboard reversible.
- Engineering-Supporting R&D:
 - Developed a baseline cost analysis for regeneration of AB that is between \$7-8/kg AB.
 - Developed cost analyses of most promising first fill pathways to prepare sodium borohydride and AB.
 - Developed improved resource reserves for borax minerals for both domestic and foreign sources indicating that there is no barrier to transition to boron fuels.

- Collaborated with Argonne National Laboratory in estimation of regeneration pathways energy efficiency.

Introduction

Chemical hydrogen storage involves storing hydrogen in molecular chemical bonds where an on-board chemical reaction is used to release hydrogen. Currently, the resulting spent fuel may be regenerated off-board using chemical processing. In addition to the importance of on-board storage capacity and hydrogen release rates, the energy efficiency of the off-board regeneration of spent fuel is a key contributor to the overall energy efficiency of the fuel cycle. Chemical hydrogen storage provides a diversity of options to enable hydrogen for transportation as well as other niche and stationary applications, and could also be used for hydrogen delivery where it offers the opportunity for a liquid or solid fuel infrastructure with the potential for no direct hydrogen handling by the consumer.

During the four years of this project, CHSCoE researchers have made substantial strides toward developing nitrogen-boron based molecular hydrogen storage compounds that can meet DOE technical targets for on board hydrogen storage. The B-N materials, such as AB and related compounds, have unique chemical properties that enables facile hydrogen release at temperatures around 100°C using a number of approaches that give rise to high rates of release. The CHSCoE has also made dramatic strides in demonstrating that spent fuel from AB may be chemically regenerated off-board. Recent process modeling work from our partner Dow Chemical (formerly of Rohm and Haas) has shown that recycle may be done with an initial estimated cost of \$7-8/kg of AB. Recent discoveries of more effective regeneration chemistries may lower this cost further.

Approach

The overall Center approach capitalizes on its broad spectrum of expertise ranging from chemical synthesis and characterization to catalysis to chemical engineering to molecular modeling and simulation to carry out research and development (R&D) in chemical hydrogen storage. The Center's activities fall into four general areas.

1. Hydrogen Release from Ammonia Borane.

This activity is populated by a number of Center partners, and is directed at developing processes for the release of hydrogen from AB. The goal is to simultaneously improve the quantity of hydrogen released while improving the rate of hydrogen

release at the lowest temperatures achievable, and with mitigation of foaming or the release of volatile byproducts that could be deleterious to the eventual utilization of the hydrogen in for example, a fuel cell.

2. **Regeneration of Spent Fuel.** This activity is directed at the energy and chemically efficient regeneration of spent fuel that arises from dehydrogenation of AB. This represents a majority of the current work being performed within the Center. The Center's regeneration efforts are directed at digesting of the spent fuel to a readily chemically processable material, then adding hydrogen to this material, and recycling any auxiliary components required along the to provide for a chemically integrated spent fuel to fuel regeneration loop.
3. **Materials Discovery.** Much of the Center's focus is on developing AB as a hydrogen storage material. The Center maintains a smaller research effort to discover other potentially useful storage materials. These areas are currently focused on developing storage materials that release hydrogen less exothermically than AB, with the goal of discovering a material that releases hydrogen with little or no heat lost or gained. This could lead to a potentially reversible, on-board regenerable fuel.
4. **Engineering Supporting R&D.** This activity, along with theory and modeling, crosscuts all of the other activities within the Center, as engineering analyses are used to inform the R&D efforts as to what the practical implications of the systems targets entail for development of an efficient hydrogen storage system. This activity provides chemical engineering and process engineering expertise for analysis of potential hydrogen storage systems and spent fuel regeneration, and provides guidance for materials down selection processes.

The overall approach of the Center is to screen and assess concepts and ideas against a set of hierarchical criteria that are derived from the DOE technical targets for hydrogen storage.

Results

Because of space limitations, this report will describe only two of the major overarching accomplishments of the Center. More detailed and complete results from the Center's activities may be found in the individual reports of the CHSCoE partners.

Hydrogen Release. During previous years, the Center has demonstrated many compounds and processes that can release greater than 7 wt% hydrogen, with many

compounds yielding in excess of 10-13 wt% hydrogen. AB, for example, in solid form, can readily release 13-15 wt% hydrogen. The key research issue that the Center has focused on is in increasing the rate and decreasing the temperature of release. A synopsis of results from the CHSCoE is shown in Figure 1.

Using ionic liquid/AB mixtures, very high rates of hydrogen release have been determined at temperatures between 100 and 120°C, where 8 wt% hydrogen is released within two minutes at 120°C.

Using catalysts, release of hydrogen from AB may be accelerated. The University of Washington has demonstrated release of 5.8 wt% hydrogen in three minutes at 25°C. Using heterogeneous catalysts LANL researchers have demonstrated hydrogen release of 8 wt% in 120 minutes at 70°C, or in 8 minutes at 110°C.

By synthesizing metal-substituted derivatives of ammonia borane, a wide array of new metal amidoborane (M-AB) storage materials have been discovered and characterized by researchers at the Pacific Northwest National Laboratory (PNNL), LANL, and the University of Missouri. As one example, PNNL has shown that Li-AB releases 5 wt% hydrogen in 2 minutes at 100°C. Li-AB also has a very high activation energy, a feature with positive implications for adequate storage lifetimes at 50-60°C. LANL has also worked closely with Center partners at the University of Missouri to characterize the hydrogen release and thermochemical properties of aluminum-based amidoborohydride compounds being prepared at Missouri.

These are but a few examples from the Center that indicate that hydrogen release from B-N systems results in good capacity delivered at high rates. To summarize, during the last four years, Center researchers have made

FIGURE 1. Synopsis of results for the release of hydrogen from a variety of materials as a function of temperature.

FIGURE 2. Improvements in rate of hydrogen release from AB. Rates to release the first equivalent (6.5 wt%) (unshaded) and the rate to release 10 wt% (shaded) have improved 100-1,000 fold.

continuous improvements in the rates of hydrogen release from B-N materials that now are 2-3 orders of magnitude greater rate than rates reported in 2006 (see Figure 2).

Regeneration. Center researchers have previously described and/or demonstrated several chemical reprocessing schemes to convert spent fuel back to ammonia borane. The best developed scheme involves the use of thiocatechol to 'digest' the spent fuel to a more reactive form, followed by subsequent amine exchange for ammonia, and a reduction using a tin hydride. Replacing the amine with ammonia regenerates AB. Recycling the tin reagent back to tin hydride completes the cycle. LANL demonstrated lab-scale regeneration

of ammonia borane, and demonstrated the proof-of-principle recycle of tin hydride. With this information in hand, process engineers at Rohm and Haas (now Dow) performed process modeling of this regeneration scheme to obtain a baseline estimate of the cost of this process. This first analysis indicated that AB regeneration could cost as little as \$7-8/kg of AB. The analysis indicated substantial opportunities to improve both the cost and the energy efficiency of the thiocatechol regeneration scheme, particularly in the area of improved separations and reduced mass of reagents.

With this information and guidance from Dow's process analysis in hand, LANL researchers developed and demonstrated a streamlined process of potentially simpler separations, and markedly fewer steps using light weight hydrazine as digesting agent and reducing agent as shown in the right panel of Figure 3. Analysis of this process is currently being performed. With the lower mass of reagents that are required, and the simpler separations schemes, this streamlined process is may have potentially reduced cost and increased energy efficiency.

Conclusions and Future Directions

Research within the CHSCoE has demonstrated that chemical hydrogen storage may be a viable approach to on board storage. Materials with high hydrogen capacities having high rates of release, good stability, and proven recycle have been synthesized, characterized, and demonstrated in the laboratory. Preliminary baseline costs for off-board regeneration have been modeled, and may be reduced further, and energy efficiencies may still be improved.

FIGURE 3. Evolution of spent fuel regeneration schemes. Left side depicts the 'thiocatechol route'. The right panel depicts an improved, simplified regeneration process using hydrazine as digesting agent and reducing agent (Y=hydrazine).

Future work within the last year of the Center will be focused on:

- Engineering support – analyze progress with respect to key barriers, provide quantitative input to prioritization, down select processes, complete additional cost estimates.
- Regeneration – use baseline cost analysis to prioritize improvements in efficiency, cost, down-select most promising regeneration pathway.
- New materials – Continue search for reversibility in covalent materials with goal of discovering on board regenerable materials.
- Hydrogen release – Finalize optimization of catalyst, ionic liquid, additive-mediated release processes, develop and describe mitigation of impurities, complete release studies for catalytic, ionic liquid-activated, and thermolytic approaches.
- Preparation of a final report of Center activities – analyze pros/cons of materials, regeneration processes, and give final recommendations to DOE.

Special Recognitions & Awards/Patents Issued

All Awards, Patents, Publications and Presentations resulting from work within the Chemical Hydrogen Storage Center are given in the accompanying partner reports.

IV.B.1b Amineborane-Based Chemical Hydrogen Storage

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Contract Number: DE-FC36-05GO15051

Project Start Date: January 1, 2005
Project End Date: March 1, 2010

Objectives

- Develop methods for on-demand, low temperature hydrogen release from chemical hydrides that can achieve DOE targets.
- Develop high conversion off-board methods for chemical hydride regeneration.

Technical Barriers

This project addresses the following technical barriers from the Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan.

- (A) System Weight and Volume
- (B) System Costs
- (E) Charging/Discharging Rates
- (R) Regeneration Processes

Technical Targets

- Gravimetric Density: 0.045 (2007); 0.06 (2010); 0.09 (2015) kg-H₂/kg
- Volumetric Density: 0.036 (2007); 0.045 (2010); 0.081 (2015) kg-H₂/L

TABLE 1. Progress toward DOE targets: Summary of AB H₂-release studies for 80:20 and 50:50-wt% AB:BmimCl mixtures and 50:50-wt% AB:BmimCl with 5 mol% PS at 120 and 110°C.

	AB and 20 wt% BmimCl		AB and 50 wt% BmimCl		AB and 50 wt% BmimCl 5 mol% PS
	120°C Two equiv. in 52 min	110°C Two equiv. in 157 min	120°C Two equiv. in 7 min	110°C Two equiv. in 22 min	110°C Two equiv. in 9 min
Initial Rate (mol/sec)	4.4x10 ⁻⁵	1.8x10 ⁻⁵	2.3x10 ⁻⁵	8.3x10 ⁻⁶	2.1x10 ⁻⁵
Grav. density (Mat. wt%)	11.4 2.2 Equiv.	11.4 2.16 Equiv.	7.2 2.06 Equiv.	6.9 2.11 Equiv.	6.1 2.21 Equiv.
Vol. density (Kg-H ₂ /L Mat.)	0.089	0.095	0.067	0.063	0.057
H ₂ Flow Rate (g/s) per kg Material	0.47	0.193	0.08	0.056	0.119
Kg of Mat. for 0.8 mol/sec	3.4	8.4	10	29	13

Accomplishments

- Significant rate enhancements along with high mat-wt% H₂-release (up to 11.4%) were demonstrated with 20 wt% ionic-liquid/ammonia borane (AB) mixtures at 110°C.
- Base-induced H₂-release in ionic liquids was extended to new bases and shown to increase the release rate of the second AB H₂-equivalent.
- A variety of metals were found to catalyze AB H₂-release in ionic liquids with significant increase for the rate of loss of the first AB H₂-equivalent.
- Completion of our work on ammonia triborane resulted in a new synthesis, its definitive structural determination and the optimization of its hydrolytic H₂-release properties.
- New solid-state and in situ nuclear magnetic resonance (NMR) studies confirmed that while there are different mechanistic pathways for AB H₂-release, the final spent fuels all contain trigonal sp² polyborazylene type structures.

Introduction

The development of efficient and safe methods for hydrogen storage is a major hurdle that must be overcome to enable the use of hydrogen as an alternative energy carrier. The objectives of this project are both to develop new methods for on-demand, low temperature hydrogen release from chemical hydrides that can achieve DOE targets and to develop high-conversion off-board methods for chemical hydride regeneration.

Approach

Because of their protonic amine-hydrogens and hydridic borane-hydrogens, amineboranes such as ammonia borane, NH_3BH_3 (AB), 19.6 wt% H_2 , and ammonia triborane $\text{NH}_3\text{B}_3\text{H}_7$ (AT), 17.7 wt% H_2 , are unique when compared to other chemical hydrides in their potential ability to store and deliver large amounts of molecular hydrogen through dehydrogenation and hydrolysis reactions. In collaboration with the other Center partners Los Alamos National Laboratory, Pacific Northwest National Laboratory (PNNL), the Universities of Washington and Alabama and the Rohm & Haas Company, our approach is to develop new methods for amineborane hydrogen-release and regeneration reactions that will enable their use for chemical hydrogen storage.

Results

Hydrogen Release Studies. In order for amine boranes to be useful for hydrogen storage, methods for more controllable H_2 -release reactions must be developed. In the first years of this project, we demonstrated that chemical additives, ionic liquids and metal catalysts could each be used to significantly increase the rate and extent of hydrogen release from both AB and AT.

During the past year our completed studies on AT were published demonstrating (1) a new, efficient preparation of AT that now makes this compound easily available; (2) new crystallographic and computational studies of the solid-state structure of AT, along with a structural determination of the AT-18-crown-6 adduct, that resolves the contradictions with previous computational structural predictions; and (3) a demonstration that upon the addition of acid or an appropriate transition metal catalyst, aqueous solutions of AT rapidly release hydrogen, with 6.1 materials-wt% H_2 -release being achieved from a 22.7-wt% aqueous solution of AT at room temperature in the presence of 5 wt%-Rh/ Al_2O_3 (1.1 mol% Rh).

One the major objectives of last year's work was to collect detailed kinetic data, with the aid of a PNNL-designed automatic gas burette, for the H_2 -release from a variety of ionic liquid-based systems in order to identify the optimal temperatures and compositions for these systems. Important findings resulting from these studies are summarized in Table 1 and Figures 1-3.

The H_2 -release studies in Figure 1 of the temperature dependence of the reactions of 50:50-wt% AB:bmmCl mixtures demonstrated that dramatic rate enhancements for H_2 -release are possible with only a modest increase in temperature. Thus, at 110°C, over 2 H_2 -equivalents are released in only ~20 min.

Our studies (Figure 2) of 80:20-wt% AB:bmmCl mixtures at various temperatures showed that significant

FIGURE 1. H_2 -release data collected on the automated gas-burette for the reactions of 50:50-wt% AB:BmimCl at different temperatures.

rate enhancements could still be achieved, with over 1.5 equiv of H_2 being released during the first 5 min at 110°C. This decrease in the amount of ionic-liquid then provides, as indicated in Figure 2, a significant increase in the materials-wt% H_2 that can be attained with these systems.

As shown in Figure 3, our gas-burette studies also demonstrated that metal-catalyzed AB H_2 -release can be attained with systems employing a variety of different ionic-liquids and metals.

Both solution and solid-state NMR studies during the last year revealed important details of both the mechanism of H_2 -release in ionic liquids and the nature of the final spent fuel products. As shown in Figure 4, solid-state ^{11}B NMR studies by Penn students at the PNNL NMR facility characterized the steps and intermediates in the Proton Sponge promoted H_2 -release from AB. The bottom spectrum shows the initial formation of both the diammoniate of diborane and sp^3 -hybridized polyaminoborane polymers. However, as the reaction progresses, the low field peak near 30 ppm that is characteristic of sp^2 -hybridized polyborazylene-type materials progressively grows until after the release of two equivalents of H_2 (top spectrum) only unsaturated $\text{B}=\text{N}$ sp^2 products are present. These NMR studies thus strongly favor a dehydrogenation process involving H_2 -elimination from adjacent polyaminoborane BH and NH groups to produce $\text{B}=\text{N}$ unsaturated polyiminoboranes that further react to form cross-linked sp^2 -bonded polyborazylene materials.

Ammonia Borane Regeneration. The efficient regeneration of ammonia borane from spent fuel BNH_x is one of the most challenging problems that will have to be overcome in order to utilize AB-based hydrogen storage systems. The development of a general regeneration process is made complicated by the fact that, depending upon the conditions and extent of H_2 -release, a variety of molecular, polymeric and/

FIGURE 2. H_2 -release data collected on the automated gas-burette for the H_2 -release reactions of 80:20-wt% AB:bmimCl mixtures at different temperatures.

FIGURE 3. H_2 -release data collected on the automated gas burette for metal-catalyzed AB H_2 -release reactions with 5-mol% metals at 65 °C with different ionic liquids (50wt%). A: $[Rh(COD)Cl]_2$ in bmimCl, B: $Ru(COD)Cl_2$ in bmimCl, C: $Ru(COD)Cl_2$ in bmimOTf, D: $RhCl_3$ in bmimCl, E: $[Rh(COD)Cl]_2$ in bmimOTf, F: $RuCl_3$ in bmimCl, G: $NiCl_2$ in bmimCl, H: $NiCl_2$ in bmimOTf, I: Rh powder in bmimCl, J: no catalyst in bmimCl, K: Ru powder in bmimCl.

FIGURE 4. Solid-state ^{11}B NMR studies of the products of Proton Sponge induced H_2 -release from AB leading to the formation of unsaturated sp^2 -hybridized final products.

or solid-state materials with very different chemical reactivities are formed. Thus, any viable process must both be capable of regenerating all of these spent-fuel materials and, in addition, avoid the formation of difficult to reduce intermediates (e.g. those containing boron-oxygen bonds). Studies were undertaken in the past year of new more efficient methods to convert spent fuel materials to boron trihalides. Since it has previously been reported that the $Na^+B(SO_3Cl)_4^-$ salt can be thermally decomposed to BCl_3 and SO_3 , we investigated the digestion of several types of spent fuels with chlorosulfonic acid. We have found that spent-fuels and the polyborazylene polymer could be totally digested by chlorosulfonic acid to produce a single species with NMR data consistent with the formation of the $NH_4^+B(SO_3Cl)_4^-$ salt.

Conclusions and Future Directions

As discussed in the previous section, our past studies have led to both the discovery and continued improvements of promising H_2 -release systems based on ammonia borane. These results have clearly shown that, while improvements are still necessary, many of these systems have the potential to achieve DOE hydrogen-storage goals. During the final year of the Center, we plan to:

- Complete H_2 -release studies for: (1) ionic-liquid/AB mixtures at different temperatures, (2) base-initiated ionic-liquid/AB mixtures, and (3) metal-catalyzed ionic-liquid/AB.
- Complete the optimization of the temperature/weight-ratios for ionic liquid based H_2 -release.
- Continue to develop and optimize new chemical-promoter systems with improved H_2 -release rates.
- Explore the activities of non-precious metal catalysts in ionic liquids for improving the rate of AB H_2 -release.
- Take advantage of synergistic mechanisms to improve H_2 -release rates.
- Explore alternative methods for the formation of boron trihalides.
- Explore, with Center partners, the development of hybrid regeneration methods.

FY 2009 Publications/Presentations

Publications

1. L.R. Alden, C.P. Griffin and L.G. Sneddon "Metal-Catalyzed Hydrogen Release from Ammonia Borane in ionic Liquids" *Prepr. Sym., ACS Div. Fuel Chem.* **2008**, 53, 670-671.

2. D. Himmelberger, M. Bluhm and L.G. Sneddon "Proton Sponge Induced Release from Ammonia Borane in Ionic Liquids" *Prepr. Sym., ACS Div. Fuel Chem.* **2008**, 53, 666-667.
3. C.W. Yoon, P.J. Carroll and L.G. Sneddon "Ammonia Triborane: A New Synthesis, Structural Determinations and Hydrolytic Hydrogen-Release Properties" *J. Am. Chem. Soc.* **2009**, 131, 855-864.
4. D. W. Himmelberger, C.W. Yoon, M.E. Bluhm, P.J. Carroll and L.G. Sneddon "Base Promoted Ammonia Borane Hydrogen Release" submitted.

Presentations

1. L. Alden, C.P. Griffin, and L.G. Sneddon "Metal Catalyzed Hydrogen Release from Ammonia Borane in Ionic Liquids" National American Chemical Society Meeting, Philadelphia, August, 2008.
2. D. Himmelberger, M. Bluhm and L.G. Sneddon "Proton Sponge Induced Hydrogen Release in Ionic Liquids" National American Chemical Society Meeting, Philadelphia, August, 2008.
3. L.G. Sneddon "Amineborane Based Chemical Hydrogen Storage" invited lecture at the International Meeting on Boron Chemistry Barcelona, Spain, September 2008.
4. L.G. Sneddon "Amineborane Based Chemical Hydrogen Storage" DOE Tech Team Meeting, Detroit, Michigan, March 2009.
5. L.G. Sneddon "Amineborane Based Chemical Hydrogen Storage" DOE Hydrogen Annual Merit Review Meeting, Washington DC, May 2009.
6. D. Himmelberger, L. Alden and L.G. Sneddon "Ionic Liquid Mediated Ammonia Borane H₂-Release" National American Chemical Society Meeting, Washington, DC, August, 2009.
7. E. Berkeley, L. Alden and L.G. Sneddon "Metal Catalyzed Ammonia Borane Dehydrogenations in Ionic Liquids" National American Chemical Society Meeting, Washington, DC, August, 2009.

IV.B.1c Chemical Hydrogen Storage R&D at Los Alamos National Laboratory

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Start Date: February 1, 2005

Projected End Date: September 30, 2010

Objectives

- Provide preliminary cost analysis of LANL regen process.
- Develop and demonstrate heterogeneous catalysts and continuous flow reactor operation.
- Develop liquid ammonia borane (AB) fuels and increase rate and extent of hydrogen release.
- Identify and demonstrate new materials and strategies for near-thermoneutral hydrogen release (ΔG° ideally no less negative than ca. -0.8 kcal/mol).
- Develop materials and processes to minimize gas-phase impurities, and demonstrate adequate purity of hydrogen stream.
- Lead most and coordinate all Chemical Hydrogen Storage Center of Excellence efforts and collaborative projects, and communicate recommendations to the Hydrogen Storage Engineering Center of Excellence.

Technical Barriers

This project addresses the following technical barriers from the Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan (MYRDDP):

- (A) System Weight and Volume
- (B) System Cost

- (C) Efficiency
- (D) Durability/Operability
- (E) Charging/Discharging Rates
- (K) System Life-Cycle Assessments
- (R) Regeneration Processes

Technical Targets

While all of the relevant targets detailed in the DOE MYRDDP will be addressed, our main emphasis focuses on the material requirements. The Center has developed interim technical guidelines to facilitate down-selection of promising materials for further development. The Center's key criteria for down-selection of storage materials include gravimetric and volumetric hydrogen capacities, as well as hydrogen release rate and temperature. The Center's criteria for materials down-selection, which are mapped to the DOE technical targets for storage systems, are tabulated in Table 1. Gravimetric capacity of materials must exceed 7 wt%, with the potential to exceed 9 wt. The latter value was determined via an analysis of Millennium Cell's very aggressive process design for hydrogen release from aqueous sodium borohydride. The goal for temperature is for hydrogen release to occur with high rate below 100°C , with an interim goal of release occurring at high rates below 120°C . The Center's criterion for the rate of hydrogen release, 0.02 g H_2 /s/kW, is the DOE 2010 target. A tabulation of all of the Center's interim targets are published in the Center's 2008 annual report, available at http://www.hydrogen.energy.gov/annual_progress08_storage.html#b.

TABLE 1. Technical Targets for Storage Systems

Criterion	Description	Metric
Material wt%	Max	> 7 wt% H_2
Potential to Regenerate On-Board	Potential to rehydrogenate spent fuel directly	yes/no/potential
Regenerable	Ability to chemically reprocess fuel offboard	yes/no/potential
Acceptable Phase Change	Problematic liquid to solid phase change	yes/no/potential
Acceptable Release H_2 Rate	Maximum rate of hydrogen release	> 0.2 g H_2 /s/kW
Stable Material $< 50^\circ\text{C}$	Stable in fuel tank $< 50^\circ\text{C}$ to H_2 release, or decomposition	yes/no/potential
Temperature of Release	Demonstrated, or potential for release at $T < 100^\circ\text{C}$	$< 200^\circ\text{C}$

The targets for regeneration of spent fuel include an interim target of 40% energy efficiency, with an ultimate goal of 60% energy efficiency, with chemical efficiencies approaching 100%, e.g. minimum losses to byproducts.

Accomplishments

- Prepared new storage materials that have lower exothermicity, higher rates to higher extents of release at lower temperatures compared to ammonia borane, with many compounds exceeding 2010 targets.
- In collaboration with Ottawa University, discovered additional liquid fuel compositions with liquid range to -30°C.
- Discovered heterogeneous base metal catalysts for hydrogen release from ammonia borane. These catalysts have been prepared and demonstrated to have high rates of release to >9 wt% H₂ at 70°C, potentially exceeding DOE technical targets.
- Demonstrated all individual steps in an AB spent fuel regeneration cycle having an overall thermodynamic efficiency of 80%, and with overall ‘once through’ chemical yield exceeding 70% conversion of spent fuel to AB in an integrated process.
- Designed, fabricated, and demonstrated flow reactor for catalyst screening and process development
- Assembled and made operational a hydrogen stream purity analysis system to identify and quantify impurities in H₂ streams.
- Polymer electrolyte membrane fuel cell apparatus for hydrogen stream purity testing has been assembled and is operating for testing of effects of impurities from chemical hydrogen release compounds.
- Provided ultra-pure ionic liquids and modified electrodes to support the Penn State University effort on electrochemical regeneration of borate to borohydride to complete Phase 1 research and development (R&D) on sodium borohydride regeneration.

Introduction

Chemical hydrogen storage involves storing hydrogen in molecular chemical bonds where an on-board chemical reaction is used to release hydrogen. Currently, the resulting spent fuel may be regenerated off-board using chemical processing. In addition to the importance of on-board storage capacity and hydrogen release rates, the energy efficiency of the off-board regeneration of spent fuel is a key contributor to the

overall energy efficiency of the fuel cycle. Chemical hydrogen storage provides a diversity of options to enable hydrogen for transportation as well as other niche and stationary applications, and could also be used for hydrogen delivery where it offers the opportunity for a liquid or solid fuel infrastructure with the potential for no direct hydrogen handling by the consumer.

Researchers at LANL are advancing a number of integrated projects involving the development of materials, catalysts, catalytic processes, and new concepts for hydrogen release and regeneration of spent fuels, as well as the development of engineering feasibility of the processes. In addition, Los Alamos hydrogen storage research benefits from productive interactions with theory collaborators across the Center at the University of Alabama, the University of California, Davis, the University of Missouri, the University of Pennsylvania (Penn), Pennsylvania State University, the University of Washington, Rohm and Haas, U.S. Borax, and the Pacific Northwest National Laboratory (PNNL). These partners collectively work on four major areas of R&D in chemical hydrogen storage: (1) hydrogen release from AB, (2) regeneration of spent fuel, (3) new materials discovery, and (4) engineering supporting R&D. Additionally, the Center is also working on ‘first-fill’ R&D to assess processes to provide the first load of a boron-containing fuel derived from mineral borates, and with U.S. Borax in assessing domestic and foreign borate resources and reserves. Los Alamos participates in all of these activities either by contributions to laboratory research, or in coordinating the R&D efforts among the partners, and in providing Center-wide communications among the various areas of R&D to keep all partners apprised of progress and issues.

Approach

LANL contributes to collaborative experimental projects in all areas of the Center’s efforts, primarily through investigations of storage materials chemistry and reactivity, experimental evaluation of the limits of capacity, release rates, and regeneration efficiencies, as well as development of new chemistry and catalytic processes and optimization of promising systems. In work on (1) *hydrogen release from AB*, LANL’s approach is to develop liquid compositions containing ammonia borane, and to develop mechanistic information to guide heterogeneous catalyst discovery for hydrogen release from AB and AB-like liquid systems. In the area of (2) *spent fuel regeneration*, LANL’s approach is to optimize the thiocatechol route to the digestion, reduction, and recycle of reagents to complete a spent fuel regeneration process, and work closely with Dow (formerly Rohm and Haas) process modelers to develop preliminary baseline cost and efficiency analyses. This involves closely working

with Penn and PNNL, who are working on separate approaches to spent fuel regeneration, and also with the University of Alabama that provides theory and modeling, and thermodynamics calculations of spent fuel regeneration chemistries. In the area of (3) *new materials discovery*, LANL's role is to work with International Partnership for the Hydrogen Economy (IPHE) partners in synthesizing, characterizing, and testing metal amidoborane compounds for hydrogen release, as well as in assessing other potential new hydrogen storage materials concepts. In the area of (4) *engineering supporting R&D*, LANL contributes to the Center's activities by performing experimental work that allows for engineering assessments of chemical hydrogen storage processes to be analyzed. LANL's engineering effort designs, fabricates, and operates chemical reactor systems for assessing continuous hydrogen release processes, as well as systems that analyze for potential gas impurities that may impact the operation downstream devices such as fuel cells. LANL's engineering effort also assists the development of criteria for hydrogen storage materials, an activity that informs the materials development and spent fuel regeneration efforts. LANL is a member of the Hydrogen Storage Engineering Center of Excellence lead by Savannah River National Laboratory, and has the task of helping to coordinate input into the design and development of subscale prototypes of chemical hydrogen storage systems.

Results

1. Hydrogen Release from AB

Research has continued on heterogeneous catalytic release of hydrogen from ammonia borane, AB. The focus has been on finding additional non-precious metal catalysts, and achieving higher rates to higher capacities at lower temperatures.

Figure 1 shows the recent results on hydrogen release from AB at 70°C catalyzed by several different types of heterogeneous catalysts derived from first row transition metal cations on a support. The best non-precious group metal catalyst has activity approaching the Pt catalysts described last year. Catalyzed dehydrogenation at higher temperatures increases the rate and capacity substantially, as shown in Figure 2.

To enable catalytic release, one must have a liquid fuel. LANL began work on liquid amine borane/AB mixtures last year. This year, working with Prof. Tom Baker at the University of Ottawa, we have found that sec-butyl amine borane/AB mixtures remain liquid at room temperature before and after catalytic dehydrogenation. Further work as a function of ratio of reagents and temperatures is ongoing.

2. Regeneration of Spent Fuel

LANL's work in regeneration of spent fuel focused on optimizing the thiocatechol route described previously, and working with Dow (formerly Rohm and Haas) to perform the process modeling necessary to develop a preliminary baseline cost analysis of spent fuel regeneration for AB (see our partner's annual report from Dow). Several process improvements were demonstrated in the lab, and incorporated into the cost analysis. Major improvements were demonstrated in the use of a 'lean' digestion that minimizes losses of reducing agent, optimization of the ligand exchange/reduction steps, and final separation of AB from the reaction mixture. Upon completion of the cost analysis by Dow, several key features to reduce cost and improve efficiency were apparent. Major improvements were potentially available from reducing the overall mass flow of reagents that was responsible for significant cost and energy inputs. The reducing agent is one key contributor to overall mass, as is the digesting agent. Another potential improvement was to combine steps whenever possible.

FIGURE 1. Base Metal Catalyzed Dehydrogenation of AB at 70°C

FIGURE 2. Catalyzed and Uncatalyzed Hydrogen Release from AB at 70 and 110°C

Subsequent laboratory research led to the discovery of two new, simplified spent fuel regeneration schemes that are shown in Figure 3. These schemes involve hydrazine, N_2H_4 , a light weight reducing agent. One option is direct digestion/reduction using hydrazine in a single step, that produces AB, hydrazine borane complex, and a small quantity of a material that may be $B(N_2H_3)_3$, but this has not been positively determined yet. The hydrazine borane complex may be converted to AB with the addition of ammonia, the topic of current investigations. An alternative pathway is also shown in Figure 3, and that is by way of digesting the spent fuel with thiocatechol as previously known, followed by reduction of the thiocatechol borane ammonia complex with hydrazine to yield once again AB, hydrazine borane, and the unidentified byproduct thought to be $B(N_2H_3)_3$.

Either of these hydrazine pathways results in simplified processing, reduced mass, and more straight forward separations. It is thought at this point that this should result in reduced cost and improved energy efficiency relative to the thiocatechol/tin hydride route previously described.

3. New Materials Discovery

LANL's efforts in new materials discovery have focused on discovering compounds that release hydrogen with near thermoneutrality. AB releases hydrogen exothermically at around 6-8 kcal/mole AB. Because of these energetics, dehydrogenated AB cannot be directly rehydrogenated using hydrogen pressure. In order to regenerate with reasonable pressures of hydrogen, hydrogen release from a storage material should not be more exothermic than approximately 1 kcal/mole.

FIGURE 3. New Schemes for Regeneration of AB from Spent Fuel Using Hydrazine

Los Alamos researchers are collaborating with partners at PNNL, and IPHE partners in the UK and New Zealand to explore and develop metal derivatives of AB. The resulting metal amidoboranes have been shown to release hydrogen at lower temperatures, but at higher rates and with the release of fewer volatile contaminants. As an example, the thermal release profile for potassium amidoborane, KAB, is shown in Figure 4, top panel. The top panel shows the weight loss curve, and the mass spectrum of the gas evolved. The concentration of gas impurities is much lower than found for the thermolysis of pure ammonia borohydride, AB. The bottom panel of Figure 4 indicates the thermochemistry of hydrogen release indicating that there is an endothermic event coupled with an overall exothermic event at the release temperature of around 100°C. LANL has recently characterized the thermochemical properties of the series of M-AB compounds for M= Li, Mg, Ca, K, and Al (prepared by our partners at the University of Missouri). These results are summarized in Table 2. While the thermochemical

FIGURE 4. Top panel – Thermal gravimetric analysis-mass spectrometry (TGA-MS) of release of hydrogen from potassium amidoborane. Bottom panel – thermochemistry of a series of metal amidoborane storage materials.

TABLE 2. Thermochemical Properties of the Series of M-AB Compounds for M= Li, Mg, Ca, K, and Al

Compound	Normalized 1 st exotherm J/g (onset/°C)	Normalized 2 nd exotherm J/g (onset/°C)	Normalized 3 rd exotherm J/g (onset/°C)	On Board Regeneration
Li AB	-621.9 (77)*			No
KAB	+70 (71)	-48.6 (75)		No
Mg (AB) ₂	-6.7 (78)	-188 (108)		No
Ca(AB) ₂	-102 (101)	-56 (120)		No
Al(AB) ₃	-38.5 (66)	-5.1 (106)	-5.9 (154)	No

properties, and the hydrogen release temperatures show a good deal of diversity, the thermodynamics of hydrogen release are still too exothermic to enable direct rehydrogenation using H₂ gas pressure, and so to date, no materials have been discovered that can be directly regenerated on board.

4. Engineering Supporting R&D

Engineering supports all of the decision making within the Center to drive R&D towards the most promising near-term solutions. In addition to many of engineering activities described above, LANL is currently working on bringing a previously designed an fabricated flow reactor system into operation to begin to measure steady state kinetics of catalytic dehydrogenation of liquid AB systems. This system will also be used to address the measurement of any catalyst deactivation or poisoning effects during reaction under a variety of conditions.

A major activity of this task during the past year was to interact with both Dow and with Argonne National Laboratory researchers on providing data and experimental support for the process analysis efforts both on regeneration baseline cost estimates and our upcoming work on an estimate of an on-board hydrogen release energy efficiency estimate.

Another portion of the engineering support task was to begin to gather the data on detection of any gas-phase impurities from chemical hydrogen storage materials and processes. Systems using gas-phase infrared spectroscopy and mass spectroscopy detection of potential impurities such as diborane, ammonia, borazine, among others, in the evolved hydrogen have been developed. Numerous release materials and processes have been qualitatively characterized for gas-phase impurities. Significant differences have been observed. By way of example, LANL has worked with our partners at Penn to begin to characterize any impurities that arise from hydrogen release from ionic liquid-AB mixtures that Penn has been exploring. In this instance, no diborane is detected, however ammonia and borazine are both detected by infrared and mass

FIGURE 5. Effect of catalytic vs. thermal hydrogen release for an AB-ionic liquid mixture as determined by gas-phase infrared spectroscopy. Catalysis mitigates borazine impurities. No diborane is detected.

spectroscopy. This result is shown in Figure 5. When hydrogen release from the ionic liquid-AB mixture is performed in the presence of a catalyst, no diborane is detected, ammonia is still present, but no borazine is detected indicating that the catalyst mitigates the release of volatile borazine. Quantification of these impurities is in progress.

Conclusions and Future Directions

Research at LANL has demonstrated the use of heterogeneous catalysts for the release of hydrogen from AB and potential liquid fuels including AB-alkylamine borane mixtures and AB-ionic liquid mixtures. With our partners at Dow, we have provided laboratory-scale demonstration of spent fuel regeneration and the information necessary to finish a preliminary baseline cost analysis of spent fuel regeneration of AB. The baseline cost for regeneration of AB from spent fuel using LANL's thiocatechol process is \$7-8/kg. This cost analysis indicated opportunities for substantial process improvements. This led to further regeneration research at LANL, and the discovery of a simplified, potentially less costly and more energy efficient process using hydrazine as both digesting agent and reducing agent. In collaboration with Center and IPHE partners, LANL has carried out the synthesis, chemical characterization, hydrogen release studies, and thermochemical characterization of additional new metal amidoborane storage materials bringing the total of such new compounds to greater than a dozen.

In Fiscal Year 2010 we will:

- Prepare fuels that meet DOE targets for operability, including storage stability.
- Identify, test metal AB derivatives (mixed metal systems) with potential for on-board regeneration.

- Identify, demonstrate additional non-precious metal heterogeneous catalyst with yet higher rates and with high durability using a continuous flow reactor that will also begin to help us address cold-start issues (supports the Hydrogen Storage Engineering Center of Excellence).
- Quantify purity of hydrogen – identification, quantification, and mitigation.
- Improve regeneration process efficiency and reduce cost.
- Confirm regeneration capability of liquid fuel mixtures with regeneration processes.
- Prepare final report.

FY 2009 Publications, Presentations, and Patents

Peer-reviewed Publications

- Efficient Regeneration of Partially Spent Ammonia Borane Fuel**, Benjamin L. Davis, David A. Dixon, Edward B. Garner, John C. Gordon, Myrna H. Matus, Brian Scott, and Frances H. Stephens, *Angewandte Chemie*, Published Online, June 9, 2009.
- Coordination of aminoborane, NH_2BH_2 , dictates selectivity and extent of H-2 release in metal-catalysed ammonia borane dehydrogenation**, Pons, V.; Baker, RT; Szymczak, NK; Heldebrant, DJ; Linehan, JC; Matus, MH; Grant, DJ; Dixon, DA, *Chemical Communications* (2008) iss.48, p.6597-6599.
- B-N compounds for chemical hydrogen storage**, Hamilton, CW; Baker, RT; Staubitz, A; Manners, I, *Chemical Society Reviews* (2009) Vol.38, iss.1, p.279-293.
- Catalytic dehydrogenation of ammonia borane in non-aqueous medium**, Shrestha, RP; Diyabalanage, HVK; Semelsberger, TA; Ott, KC ; Burrell, AK; et al., *International Journal of Hydrogen Energy*, (MAR 2009) Vol.34, iss.6, p.2616-2621.
- Formation of Benzodiazaborolanes From Borazine**, Benjamin L. Davis, Andrew D. Sutton, John C. Gordon, Daniel E. Schwarz, Brian L. Scott, David L. Thorn, *Main Group Chemistry*, *submitted for publication*.
- Recycle of Tin Thiolate Compounds Relevant to Ammonia-Borane Regeneration**, Benjamin L. Davis, Andrew D. Sutton, Koyel X. Bhattacharyya, Bobby D. Ellis, Philip P. Power, John C. Gordon, *Chemical Communications*, in preparation.
- Two-Step Regeneration of Dehydrogenated Ammonia-Borane Fuel**, Andrew D. Sutton, John C. Gordon, David D. Dixon, *Manuscript in preparation*

Symposia Proceedings

- Transition metal initiated catalytic dehydrogenation of ammonia borane in non-aqueous medium**, Shrestha, Roshan P.; Diyabalanage, Himashinie V.K.; Semelsberger, Troy A.; Burrell, Anthony K. From Preprints of Symposia - American Chemical Society, Division of Fuel Chemistry (2008), 53(2), 691-692.
- Metal derivatives of ammonia-borane: potential hydrogen storage materials**, Diyabalanage, Himashinie V.K.; Shrestha, Roshan P.; Semelsberger, Troy A.; Scott, Brian L.; Burrell, Anthony K. From Preprints of Symposia - American Chemical Society, Division of Fuel Chemistry (2008), 53(2), 672-673.

Presentations

- Chemical hydrogen storage at Los Alamos**, Gordon, John C.; Davis, Benjamin L.; Dixon, David A.; Matus, Myrna H.; Stephens, Frances H. From Abstracts of Papers, 237th ACS National Meeting, Salt Lake City, UT, United States, March 22-26, 2009 (2009), INOR-404.
- Transition metal initiated catalytic dehydrogenation of ammonia borane in nonaqueous medium**, Shrestha, Roshan L.; Diyabalanage, Himashinie V.K.; Burrell, Anthony K. From Abstracts of Papers, 236th ACS National Meeting, Philadelphia, PA, United States, August 17–21, 2008 (2008), FUEL-065.
- Metal derivatives of ammonia-borane: Potential hydrogen storage materials**, Diyabalanage, Himashinie V.K.; Shrestha, Roshan L.; Semelsberger, Troy A.; Scott, Brian L.; Burrell, Anthony K. From Abstracts of Papers, 236th ACS National Meeting, Philadelphia, PA, United States, August 17–21, 2008 (2008), FUEL-056.
- Cheap, easy, fast and selective: Optimizing catalysts for ammonia-borane dehydrogenation**, Hamilton, Charles W.; Baker, R. Tom; Shrestha, Roshan; Semelsberger, Troy A. From Abstracts of Papers, 235th ACS National Meeting, New Orleans, LA, United States, April 6–10, 2008 (2008), INOR-147.

Patents

- Process for stepwise preparation of boranes and borane complexes by reaction of boron compounds with metal hydrides**, Thorn, David L.; Tumas, William. From PCT Int. Appl. (2008), WO 2008039312 A2 20080403.
- Regeneration of Ammonia Borane From Polyborazylene**, Andrew D. Sutton, John C. Gordon, Provisional patent applications: S-116,299.
- Regeneration of Ammonia Borane From Polyborazylene**, Andrew D. Sutton, John C. Gordon, Provisional patent application S -116,318.

IV.B.1d Chemical Hydrogen Storage Research at PNNL

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Start Date: March 1, 2005

Projected End Date: September 30, 2010

Objectives

- Develop materials and methods for low temperature (<85°C) release of pure hydrogen (99.99%) from chemical hydrides that can achieve DOE targets (>90g H₂/kg and >70g H₂/l):
 - Focus on quantitative measurements of impurities in H₂.
- Develop high efficiency methods for large scale synthesis of chemical hydrogen storage materials:
 - Fabricate reactor to prepare bench scale quantities of ammonia borane (AB).
- Develop high efficiency off-board methods for chemical hydride regeneration to achieve DOE targets (60%):
 - Coordinate with Argonne National Laboratory to do preliminary efficiency analysis of regen process.
- Support collaborators through expertise in chemistry and characterization to determine the kinetics and thermodynamics of hydrogen release and regeneration of H-storage materials:
 - Work with Center partners to characterize materials and novel approaches to store and release hydrogen.

Technical Barriers

This project addresses the following technical barriers from the Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) System Weight and Volume
- (B) System Cost
- (C) Efficiency
- (E) Charging/Discharging Rates
- (R) Regeneration Processes
- (S) By-Product/Spent Material Removal

Technical Targets

Scheme 1 represents the focus of materials (ammonium borohydride, AB, diammoniate of diborane, lithium amidoborane and sodium amidoborane) currently under study and provides both the gravimetric and volumetric density of hydrogen. Table 1 presents a summary of the rates of hydrogen release, enthalpies of hydrogen release and impurities measured for various materials, temperatures and reaction conditions.

Solid phase chemical hydrogen storage materials studied

$\text{NH}_4\text{BH}_4 \rightleftharpoons \text{BNH}_x + \text{H}_2$	(240 g H ₂ /kg, 130 g H ₂ /l)
$\text{NH}_3\text{BH}_3 \rightleftharpoons \text{BNH}_x + \text{H}_2$	(195 g H ₂ /kg, 140 g H ₂ /l)
$[\text{NH}_3\text{BH}_2\text{NH}_3][\text{BH}_4] \rightleftharpoons \text{BNH}_x + \text{H}_2$	(195 g H ₂ /kg, 140 g H ₂ /l)
$\text{LiNH}_2\text{BH}_3 \rightleftharpoons \text{LiBNH}_x + \text{H}_2$	(109 g H ₂ /kg, 52 g H ₂ /l)
$\text{NaNH}_2\text{BH}_3 \rightleftharpoons \text{NaBNH}_x + \text{H}_2$	(76 g H ₂ /kg, 43 g H ₂ /l)

SCHEME 1. Materials currently under study and their gravimetric and volumetric density of hydrogen.

Accomplishments

- Scaled up AB synthesis (one-pot >95% yield, >99% purity).
- Determined stability of solution phase AB (to compare with solids).
- Quantified impurities in H₂ from AB and initiated approaches to mitigate and control.
- Optimized anti-foaming agents to retain solid state AB fuel morphology.
- Expanded studies of M-NH₂-BH₃: mechanisms of H₂ release, rates, stability studies, impurities

TABLE 1. Summary of the rates of hydrogen release, enthalpies of hydrogen release and impurities measured for various materials, temperatures and reaction conditions.

Compound	Gravimetric	Volumetric	Additive	Enthalpy	Peak Rate	Temperature	NH ₃	Bz	Notes
	g H ₂ /kg	g H ₂ /l		kJ/mol	g/s/kg	C	ppm	wt%	
NH ₃ BH ₃	194 (160)	146 (120)	none	-23	3.8	160	100-200	4-6	foams
NH ₃ BH ₃	"	"	none	-23	2.1	145	100-200	4-6	foams
NH ₃ BH ₃	"	"	none	-23	1.1	130	100-200	4-6	foams
NH ₃ BH ₃ + AF	155 (136)	117 (102)	anti foaming	-23	1.1	130	?	?	no foam
AB:MCM	"	"	scaffold (1:1)	-1 (-22)	2.8	130	100-200	<1	no foam
AB:MCM	"	"	scaffold (2:1)	-10	?	130	100-200	<1	no foam
AB:MCM	"	"	scaffold (3:1)	-12	1.9	130	100-200	<1	no foam
DADB	194 (160)	?	none	-16	1.8	145	?	?	little foam
DADB	"		none	-16	0.48	130	?	?	little foam
DADB	"		none	-16	0.2	100	?	?	little foam
NH ₄ BH ₄	240	130	none	-63	?	40	?	?	little foam
LiNH ₂ BH ₃	109	52	none	?	1.76	130	200	0	no foam
LiNH ₂ BH ₃	"	"	none	?	0.44	100	2,000	0	no foam
LiNH ₂ BH ₃	"	"	none	-2	0.08	90	2,000	0	no foam
LiNH ₂ BH ₃	"	"	none		0.01	80	2,000	0	no foam
NaNH ₂ BH ₃	76	43	none	?	0.044	80	?	0	no foam
NaMeNHBH ₃	30	?	none	?	0.043	100	?	0	no foam

Summary of rates, enthalpies and purity of hydrogen. theoretical density (measured density). Bz = borazine. ? = not yet measured, will be determined in future work. enthalpy in scaffold depends on isothermal or ramp heating

(International Partnership for the Hydrogen Economy [IPHE] collaboration).

- Developed approach to stabilize ammonium borohydride (NH₄BH₄) at room temperature.
- Demonstrated hydride transfer chemistry from 'activated' H₂ to digested fuels using non-precious metal reagents.

Approach

PNNL's approach is consistent with the philosophy Chemical Hydrogen Storage Center of Excellence. *A comprehensive understanding will enable the development of rational approaches to enhance rates of release, increase purity of hydrogen, and provide energy efficient regeneration schemes.* In addition to a focus on solid state chemical hydrogen storage, PNNL has responsibilities for theory and simulation and core science and engineering competencies within the Center. Therefore, PNNL's work within the Center is inherently multidisciplinary and highly collaborative with several of the Center partners.

PNNL has many activities including examination of mechanisms of hydrogen release from solid ABs, experimental work on the regeneration of spent ABs,

and addressing the materials handling issues associated with solid fuels. PNNL also leads the engineering activities within the Center, which are now targeted toward off-board regeneration of fuels. This group interfaces on a regular basis with DOE's Storage System Analysis Working Group.

Results

Efforts at PNNL in Fiscal Year 2009 were focused on six major tasks: (i) scale up 'first-fill' synthesis of AB, (ii) stabilizing fuels, AB for regeneration and ammonium borohydride for first fill, (iii), quantifying the concentration of impurities, NH₃ and borazine in the hydrogen released from AB, (iv) optimization of anti-foaming additives for AB fuel formulations, (v) developed mechanistic understanding of hydrogen release from IPHE materials, metal amidoboranes and (vi) expanding the database of materials to enhance understanding of hydride affinity of borate esters and donors ability of metal hydrides for regeneration chemistry.

- First-Fill – PNNL designed and fabricated a bench scale reactor to prepare AB from sodium borohydride and an ammonium salt in a single pot to provide high yields (95-99%) and high purity (>99%) AB. The design concepts and materials

properties were shared with Center partner Rohm and Haas to provide an economic analysis to compare with procedures currently used to synthesis AB for first fill applications.

- **Stabilizing Fuels** – (a) ammonium borohydride was shown to be stable at room temperature in liquid ammonia. Little work has been previously performed on this unique borohydride in the last 50 years due to the lack of stability at room temperature. (b) AB decomposes by a second order reaction mechanism in solution. It is critical for regen to develop a stabilizer additive or protect the borane with a tertiary amine. AB can thus be recovered by a trans ammonization step (see results on regeneration).
- **Hydrogen Purity from AB** – Last year we demonstrated that ca. 16.5 wt% of the hydrogen is released from AB at temperature <150°C. Analysis of the hydrogen gas suggested that two impurities, ammonia and borazine are formed in the decomposition reaction. Subsequent work was performed to quantify the impurities in the H₂ gas stream. Ammonia is formed at levels of ca. 200 ppm when >15 wt% hydrogen is released. The yield of borazine is independent of heating rate and is formed in ca. 4±2% when >15 wt% hydrogen is released from AB. By keeping temperatures below 150°C the borazine yield can be significantly reduced.
- **Anti-Foaming Agents** – Methyl cellulose at 15 wt% prevents foaming of solid pellet fuel forms. This is a significant result; in that, pellets or monolithic fuels can now be formulated that can be handled in an engineered system.
- **IPHE Materials** – Metal amido boranes have been shown to decompose to release hydrogen by a different mechanism than AB hydrogen release. There is no induction period and steep temperature dependence.
- **Regeneration** – Another key aspect of the PNNL project is chemical regeneration. The first regeneration hurdle with solids is getting the spent fuel into a chemical form where reduction chemistry can be employed. In general, this implies the fuel must be digested into a liquid solvent. In FY 2007 and early FY 2008 we showed that alcohols are suitable for this purpose. Since then PNNL has been looking at reduction chemistry to put hydrogen back into the spent material. This effectively involves making B-H bonds from the digestion product (B-OR bonds). Methods using hydrides of sodium or aluminum are known. However, the cost of regenerating these hydrides makes their use prohibitive. Therefore, PNNL has been investigating approaches using transition metal hydrides. Studies began with one of the strongest transition metal hydride donors available: bis(dimethylphosphinoethane)rhodium hydride

[HRh(dmpe)₂]. Theoretical analysis showed that B(OPh)₃ has sufficient hydride affinity to react and indeed PNNL found that HRh(dmpe)₂ does transfer H⁻ to B(OPh)₃. A process then was envisioned as shown in Scheme 2; where R is an alcohol such as *tert*.-butanol; PhOH is phenol; M is a transition metal complex. Through FY 2009 PNNL developed process flow sheets, performed proof-concept experiments, and worked to advanced understanding of factors that affect reactivity and efficiency in the process steps. PNNL has found precedent for and demonstrated all the steps individually. The remaining challenge is to develop a transition metal complex with suitable properties such that the steps can be integrated into a process. Ideally, the acidity of the MH₂ complex should be similar to the acidity of phenol and the H⁻ donor abilities of MH should be matched to the H⁻ accepting abilities of B(OPh)₃. The properties of the HRh(dmpe)₂ are not optimal in this regard. For example, the deprotonation of H₂Rh(dmpe)₂⁺ requires base that is much stronger than PhO⁻ and HRh(dmpe)₂ is a stronger H⁻ donor than is needed to reduce B(OPh)₃. Structure-reactivity trends for known transition metal complexes pointed to cobalt complexes. PNNL synthesized complexes with dmpe and other bis phosphine ligands and explored their properties and reactivities. The results show that HCo(dmpe)₂ is not strong enough of a hydride donor to transfer a hydride to B(OPh)₃. However, it readily transfers H⁻ to B(OC₆F₅)₃, which has greater H⁻ affinity compared to B(OPh)₃. Also, it transfers H⁻ to B(SPh)₃ which has an intermediate hydride affinity. On the basis of these observations and recent theoretical analyses, PNNL is examining the use of chlorophenols in place of phenol in the above process with complexes of Co.

1) Digestion

2) Transition Metal Hydride Formation

3) Hydride Transfer/Ligand Redistribution

4) Recycle

5) Ammoniation

SCHEME 2. Process Using Transition Metals Catalysts to Regenerate Spent AB Fuel

Argonne National Laboratory performed an energy and efficiency analysis of the above process. Their preliminary analysis estimated a well-to-tank efficiency of 25-47%. Scenarios leading to higher efficiencies assumed hydridic H in spent fuel may be recovered as a BH_3 adduct by the following reaction sequence:

Work is in progress to evaluate the efficiency of for recovering hydridic H in spent ammonia borane fuels which have released greater than 2 equivalents of H_2 .

Conclusions and Future Directions

In sum, FY 2009 has resulted in the continued growth in knowledge of B-N materials. We can prepare large-scale quantities of AB of sufficient purity to meet DOE stability targets. We demonstrated for the first time that ammonium borohydride can be stabilized at room temperature in ammonia solvents. This enhance stability is key to first fill engineering requirements and provides initial insight into stabilizing ammonium borohydride for storage applications. We demonstrated that concentrated solutions of AB are not stable due to the second order decomposition pathways. These insights lead to alternative approaches to stabilize boranes in the regeneration process. Additives such as methyl cellulose can prevent foaming of AB during the hydrogen release and preserve fuel form factors – critical for transferring solid fuel forms in a reactor. PNNL, in collaboration with University of California, Davis, has quantified impurities, i.e. ammonia and borazine, in the hydrogen released from solid phase AB. The work shows that borazine concentrations are not dependent on heating rate but are dependent on final temperature used to release hydrogen from solid AB. IPHE collaborations continue to provide insight into the hydrogen release properties of metal amido boranes, e.g., LiNH_2BH_3 . Mechanistic studies show that decomposition has steep temperature dependence – a valuable property for stability at 60°C and high release rates at 85°C. Also, they yield of ammonia varies dependent on reaction conditions. In AB regeneration work we have demonstrated that we can activate hydrogen at ambient temperature and pressure with transition metal hydrides. Judicious matching of the metal, the base and the borate ester will lead to optimized energy efficiency.

Future Work

- Economic analysis of first-fill AB to compare to conventional methods. Optimize a continuous process from lessons learned in batch reactor.

- Mechanistic studies of ammonia and borazine formation from AB decomposition to develop rational approach to mitigate impurities in hydrogen.
- Develop additives that reduce foaming as well as increase kinetics and decrease volatile impurities.
- Mechanistic studies of ammonia formation from IPHE materials to develop procedures to maximize hydrogen purity.
- Examine Ni and Fe metals as Hydride transfer agents in regeneration.
- Provide the Hydrogen Storage Engineering Center of Excellence with property information on solid chemical hydride species that show promise to meet optimal DOE targets.

2009 Publications

- Christopher L Aardahl, Scot D Rassat. Overview of Systems Considerations for On-Board Chemical Hydrogen Storage. *Int. J. Hydrogen Energy*. 2009, accepted.
- Doinita Neiner, Abhijeet Karkamkar, John C. Linehan, Bruce Arey, Tom Autrey, and Susan M. Kauzlarich Promotion of Hydrogen Release from Ammonia Borane with Mechanically Activated Hexagonal Boron Nitride *J. Phys Chem. C*. 2009, 113, 1098.
- Brandon Dietrich, Karen Goldberg, D. Michael Heinekey, Tom Autrey, John Linehan. Iridium-Catalyzed Dehydrogenation of Substituted Amine Boranes: Kinetics, Thermodynamics, and Implications for H_2 Storage. *Inorg. Chem*, 2008.
- Zhitao Xiong, Yong Shen Chua, Guotao Wu, Weiliang Xu, Ping Chen, Wendy Shaw, Abhi Karkamkar, John Linehan, Tricia Smurthwaite, and Thomas Autrey. Interaction of Lithium Hydride and Ammonia Borane in THF. *Chem. Comm.* 2008, DOI: 10.1039/b812576g.
- Wendy Shaw, John Linehan, Nathaniel Szymczak, David Heldebrant, Clem Yonker, Donald M. Camaioni, R. Tom Baker, Tom Autrey. In Situ Multinuclear NMR Studies of the Thermal Decomposition of Ammonia Borane in Solution. *Angew. Chem. Int. Ed.* 2008, 47, 7493.
- Feng Zheng, Scot D. Rassat, David J. Heldebrant, Dustin D. Caldwell, Christopher L. Aardahl, Tom Autrey, John C. Linehan, and Kenneth G. Rappé, Automated gas burette system for evolved hydrogen measurements. *Review Scientific Instruments* 2008, 79, 084103.
- David Heldebrant, Abhi Karkamkar, Nancy Hess, Mark Bowden, Scot Rassat, Feng Zheng, Kenneth Rappé, Tom Autrey. The Effects of Chemical Additives on the Induction Phase in Solid-State Thermal Decomposition of Ammonia Borane. *Chem. Materials*. 2008, 20, 5332.
- Zhitao Xiong, Chaw Keong Yong, Guotao Wu, Ping Chen, Wendy Shaw, Abhi Karkamkar, Tom Autrey, Martin Jones, Simon Johnson, Peter Edwards, William David. High Capacity Hydrogen Storage in Lithium and Sodium Amidoboranes. *Nature Materials*, 2008, 7, 138.

9. Mark Bowden, Tom Autrey, Ian Brown, Martin Ryan. The thermal decomposition of ammonia borane: A potential hydrogen storage material. *Current Applied Phys.* 2008, 8, 498.

2009 Presentations

1. ST Autrey Workshop on Clean Energy Technology, Tiayuan, China (Sept 2008).
2. ST Autrey LANL-NEDO-AIST Meeting on H₂ Research, San Diego, CA (Sept 2008).
3. CL Aardahl LANL-NEDO-AIST Meeting on H₂ Research, San Diego, CA (Sept 2008).
4. DJ Heldebrant Chem Department Colloquium, Queens College, Canada (Oct 2008).

5. ST Autrey Materials Science Dept Colloquium, Seattle, WA (Oct 2008).
6. WJ Shaw Materials Science Institute Workshop, Gleneden Beach, OR (Dec 2008).
7. CL Aardahl TMS2009 Meeting, San Francisco, CA (February 2009).
8. AJ Karkamkar APS 2009 Annual Meeting, Pittsburgh, PA (March 2009).
9. D Neiner ACS National Meeting, Salt Lake City, UT (March 2009).

IV.B.1e Main Group Element and Organic Chemistry for Hydrogen Storage and Activation

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Contract Number: DE-FC36-05GO15059

Start Date: January 1, 2005
Projected End Date: March 31, 2010

Objectives

- Develop new chemistries to enable DOE to meet the technical objective: *By 2010, develop and verify on-board hydrogen storage systems achieving 1.5 kWh/kg (4.5 wt%) and 0.9 kWh/L. By 2015, develop and verify on-board hydrogen storage systems achieving 1.8 kWh/kg (5.5 wt%) and 1.3 kWh/L by using chemical hydrogen storage systems.*
- Focus on novel organic and main group compounds to enable new chemistries which may be able to perform better for release and regeneration of spent fuel by improving the energy balance and to provide longer term alternatives.
- Provide computational chemistry support (prediction of thermodynamics, kinetics, spectroscopic properties, mechanisms, etc.) to the experimental efforts of the DOE Center of Excellence for Chemical Hydrogen Storage to reduce the time to design new materials and develop materials that meet the 2010 and 2015 DOE objectives. Focus on new materials, hydrogen release mechanisms, and regeneration of spent fuel processes.

Technical Barriers

This project addresses the following technical barriers from the Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan: <http://www1.eere.energy.gov/hydrogenandfuelcells/mypp/pdfs/storage.pdf>

- (A) System Weight and Volume
- (B) System Cost
- (C) Efficiency
- (D) Durability/Operability
- (E) Charging/Discharging Rates
- (I) Dispensing Technology
- (J) Thermal Management
- (R) Regeneration Processes
- (S) By-Product/Spent Material Removal

Technical Targets

Storage Parameter: DOE 2010 System Targets	Carbene/Cyanocarbon: (No-Go Decision)	Imidazolo Borane
Material Gravimetric Capacity: 4.5 wt%	Current: 2%	Current: 1% Ultimate: 7.1%
Material Volumetric Capacity: 0.028 kg/L	Current: 0.045	Current: ~0.02 Ultimate: 0.098
Dehydrogenation Rate 0.02g/s-kW	In progress	Rate of H ₂ release: 9.6 ± 0.5 M ⁻¹ s ⁻¹
Storage Efficiency Center Goal: 50% Near: Thermoneutral	Exothermic: -5 kcal/mol Ultimate: Thermoneutral	In progress

Accomplishments

- Developed approach to predict heats of vaporization (liquid heats of formation) with new atomic parameters derived from experiment (Chemical Hydrogen Center of Excellence, Los Alamos National Laboratory, Rohm & Haas). Tested against known values. Used for process simulations.
- Predicted reliable thermodynamics for thousands of compounds for release and regeneration schemes to aid in materials design and process design and simulation. Data provides guidance for experimental design and used in process simulations.

- Continued validation of density functional theory (DFT) by experiment where available and accurate molecular orbital (MO) theory (coupled cluster theory with single and double excitations plus a perturbative correction for triple excitations/ complete basis set limit).
- Significant advances in reliable predictions of the thermodynamics of new chemical hydrogen storage systems to help groups focus experimental efforts. Example: Calculated $C_xB_yN_zH_{12}$ ($x+y+z = 6$) chemistries – new aromatic compound C_4BNH_6 .
- Predicted properties of borane-imidazole complexes with potential to improve release kinetics.
- Predicted energetics for methyl substituted amine-boranes for improved fuel properties (liquids) and improved thermochemistry. Also for amine exchange reactions for regeneration.
- Developed new thermodynamic models for metal substituted $M/BH_2NH_3^-$ and $M/NH_2BH_3^-$ complexes. $M = Li, Mg, Ca, Al, Si, C, P, N, Ti$ (Chemical Hydrogen Center of Excellence and University of Missouri).
- Predicted kinetics for a range of H_2 release processes.
 - Extended work to alanes. Identified multiple transition states and new complexes. Interact with Metal Hydride Center of Excellence.
- Carbene experimental work completed. (No-Go decision).
- Exploring different carbon, nitrogen, boron and hydrogen compounds based on BH_3 -imidazole structure computationally and new routes to ammonia borane (AB).

Introduction

Our goal is to develop new chemistries to enable DOE to meet the technical objective: *By 2010, develop and verify on-board hydrogen storage systems achieving 1.5 kWh/kg (4.5 wt%) and 0.9 kWh/L. By 2015, develop and verify on-board hydrogen storage systems achieving 1.8 kWh/kg (5.5 wt%) and 1.3 kWh/L by using chemical hydrogen storage systems.* We are: providing computational chemistry support (thermodynamics, kinetics, properties prediction) to the experimental efforts of the DOE Chemical Hydrogen Storage Center of Excellence to reduce the time to design new materials and develop materials that meet the 2010 and 2015 DOE objectives. The computational chemistry effort broadly supports the Center in the discovery of new materials, the prediction of novel

hydrogen release mechanisms, and the design of efficient regeneration processes. We are using experimental approaches to synthesize new organic/main group compounds with the appropriate release kinetics and thermodynamics and that can be readily regenerated.

Approach

To achieve the goals described in the Introduction, we are:

1. Using highly accurate and validated first principles computational chemistry approaches on advanced computer architectures to predict the electronic structure of molecules to obtain thermodynamic and kinetic information in support of the design of hydrogen storage materials and of regeneration systems. Our focus is on the design of hydrogen storage materials and of catalysts to effect easy release of H_2 as well as efficient regeneration schemes. We use a combination of validated MO theory and DFT based on our accurate benchmark calculations. We are developing methods to predict the properties of the molecules under study in condensed phases. The key issue is the accuracy/reliability of the models for the real systems.
2. Developing new compounds and approaches to release hydrogen from organic and main group compounds based on new chemistries. The focus of this effort is to demonstrate proof of concepts and key reactions. The key experimental issues are minimizing the weight by eliminating substituents or changing them into components that can store H_2 while maintaining kinetic and thermodynamic properties and demonstrating H_2 release reactions under expected operating conditions.
3. Using a combined computational/experimental goal to develop new concepts to improve energy balance which is relevant for the ease of H_2 release and regeneration of H_2 storage system. We are continuing to develop computational thermodynamic and kinetic approaches for chemical H_2 storage based on exploiting ΔH and ΔG coupled with Le Chatelier's principle to manage H_2 addition and release in chemical compounds.

For the experimental effort, there are close interactions with Los Alamos National Laboratory. The computational effort supports the entire Center.

Results

Substantial progress has been made this year in terms of the computational and experimental efforts.

Examples of computational results include:

1. The prediction of reliable thermodynamics for thousands of compounds for release and

regeneration schemes to aid in materials design and process design and simulation. All of our thermodynamic values have been updated due to a new heat of formation of the B atom. We developed and tested extensively a validated, new approach for the prediction of molecular properties in condensed phases with new atomic parameters to predict T_{BP} , ΔH_{vap} , and $\Delta H(liquid)$ which uses accurate calculated $\Delta H(gas)$ and is based on the computational method CONductor like Screening MOdel for Realistic Solvents (COSMO-RS). Thermodynamic and kinetic data was provided to experimentalists to guide their choice of experiments. Thermodynamic and property data was provided to Rohm & Haas (Dow) for the chemical process simulations at the plant level for regeneration and first fill. An example of such data is shown in Figure 1. We developed a good model for the prediction of the thermodynamics of spent fuel for “BNH₂” and “BNH”. Reliable estimates of maximum process efficiency in terms of thermodynamics was made using equation (1)

$$\frac{(\text{Equiv. H}_2 \text{ stored})(57.8)}{(\text{Equiv. H}_2 \text{ used})(57.8) + \sum (\Delta H_{\text{endo}}) - (\% \text{ heat recovery}) \sum (-\Delta H_{\text{exo}})} = \text{efficiency} \quad (1)$$

- We have made significant advances in reliable predictions of the thermodynamics of new H₂ chemical hydrogen storage systems including those based on the product C₄BNH₆. A reliable heat of formation of C₄BNH₆ at 298 K of 3.0 kcal/mol was predicted and the compound is shown to have a resonance stabilization energy of 21 ± 2 kcal/mol in comparison to a value of 34.1 kcal/mol for benzene

obtained in the same way (collaboration with the University of Oregon).

- We have extended our computational studies to complexes of borane amines bonded to main group compounds and transition metals. An important set of main group and transition metal complexes are derived from binding (NH₂BH₃)⁻ to a cationic center such as Li⁺, Ca²⁺, Al³⁺ or Ti⁴⁺ to form the respective complexes Li(NH₂BH₃), Ca(NH₂BH₃)₂, Al(NH₂BH₃)₃, and Ti(NH₂BH₃)₄. We are completing such calculations as well as on the reverse compositions based on M-(BH₂NH₃)_n. Calculations have been done for a number of molecular systems at the DFT (B3LYP) and MO theory (G3MP2) levels. An example is shown in Figure 2.
- We have continued our studies of catalytic H₂ release processes and predicted orders of magnitude improvement in kinetics. This work has led to new understanding of alane chemistries for metal hydride regeneration schemes based on amine complexation where we have identified multiple transition states and new complexes. This has also been extended to reactions of hydrazine as shown in Figure 3.

Experimental advances include:

- A borane transfer process has been developed based on a du Pont patent (No. 5,034,464; A.J. Arduengo, July 23, 1991). The new process facilitates transfer of a BH₃ unit from sodium borohydride to a variety of amines (including ammonia) with the intermediary of a proprietary borane transfer agent as shown in Figure 4. The overall yield in early experiments is 80–95%.

Reactor 1:

$\Delta H(\text{kcal/mol})$		
Digestion	(1a) BNH + 1.5 C ₆ H ₄ (SH) ₂ → 0.5 HB(C ₆ H ₄ S ₂) ₂ NH ₃ + 0.5 (NH ₄)B(C ₆ H ₄ S ₂) ₂	8.6
Undesirable:	(1b) C ₆ H ₄ (SH) ₂ + HB(C ₆ H ₄ S ₂) ₂ NH ₃ → (NH ₄)B(C ₆ H ₄ S ₂) ₂ + H ₂	22.9

Reactor 2:

Reduction:	(2a) 0.5 (NH ₄)B(C ₆ H ₄ S ₂) ₂ + 0.5 Bu ₃ SnH → 0.5 HB(C ₆ H ₄ S ₂) ₂ NH ₃ + 0.5 C ₆ H ₄ (SH)(SSnBu ₃) ₂	-18.3
Amine Exchange:	(2b) HB(C ₆ H ₄ S ₂) ₂ NH ₃ + Et ₂ NH → HB(C ₆ H ₄ S ₂) ₂ NHEt ₂ + NH ₃ (g)	1.6
Reduction:	(2c) HB(C ₆ H ₄ S ₂) ₂ NHEt ₂ + 2 Bu ₃ SnH → Et ₂ NHBH ₃ + C ₆ H ₄ (SSnBu ₃) ₂	9.5
Net:	(2d) 0.5 HB(C ₆ H ₄ S ₂) ₂ NH ₃ + 0.5 (NH ₄)B(C ₆ H ₄ S ₂) ₂ + Et ₂ NH + 2.5 Bu ₃ SnH → Et ₂ NHBH ₃ + NH ₃ + 0.5 C ₆ H ₄ (SH)(SSnBu ₃) ₂ + C ₆ H ₄ (SSnBu ₃) ₂	-7.2
Undesirable:	(2e) C ₆ H ₄ (SH) ₂ + Bu ₃ SnH → C ₆ H ₄ (SH)(SSnBu ₃) ₂ + H ₂	-13.7
	(2f) C ₆ H ₄ (SH)(SSnBu ₃) ₂ + Bu ₃ SnH → C ₆ H ₄ (SSnBu ₃) ₂ + H ₂	-5.0
Net:	(2g) C ₆ H ₄ (SH) ₂ + 2 Bu ₃ SnH → C ₆ H ₄ (SSnBu ₃) ₂ + 2 H ₂	-18.7

Reactor 3

Ammoniation:	(3) Et ₂ NHBH ₃ + NH ₃ (l) ⇌ H ₃ NBH ₃ + Et ₂ NH	-7.3
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Reactor 4:

Metal Recycle:	(4a) C ₆ H ₄ (SSnBu ₃) ₂ + 2 H ₂ → C ₆ H ₄ (SH) ₂ + 2 Bu ₃ SnH	18.7
	(4b) 0.5 C ₆ H ₄ (SH)(SSnBu ₃) ₂ + 0.5 H ₂ → 0.5 C ₆ H ₄ (SH) ₂ + 0.5 Bu ₃ SnH	6.8

FIGURE 1. Thermodynamics in kcal/mol for Los Alamos National Laboratory AB regeneration pathway. Thermodynamic data enables process simulations and cost estimates.

FIGURE 2. Dehydrogenation pathways and B-N bond dissociation energies for the aluminum borane amines at the B3LYP/DZVP2 level. $\Delta H(298)/\Delta G(298)$ in kcal/mol are given.

FIGURE 3. Energy profiles showing the pathways for H_2 -release from $AlH_3 + BH_3 + N_2H_4$. Relative energies in kcal/mol at the CCSD(T)/aVTZ + ZPE level. Small balls are H atoms.

2. A novel hydrogen activation process has been developed which showed that Lewis acid-base pairs need not be “frustrated” in their reactivity towards

activating H_2 . Reaction can occur at temperatures as low as $-80^\circ C$. We established that the interaction of H_2 with the electrophile is a key step in the

FIGURE 4. Schematic of borane transfer technology for new approach to the synthesis of first fill ammonia borane.

activation process. Electrophiles to replace our initial $\text{Fe}(\text{CO})_5$ reactant such as BBr_3 , $\text{B}(\text{OCH}_3)_3$, 1-bora-adamantane, and trityl cation reacting with an imidazolydene nucleophile have been investigated. The BBr_3 and trityl cation work. This provides another route to make H_2 into a proton and hydride (like BH_3NH_3) or the Pacific Northwest National Laboratory (PNNL) work for regeneration cycles.

3. We have continued to study hydrogen elimination from azolium borohydrides (polymeric amine borane analogs) from both a computational and experimental viewpoint. The reduced basicity of heterocyclic systems containing multiple nitrogens is such that amine-borane adduct formation from the neutral is difficult and the stability of the initially formed adducts is marginal. Hydrogen evolution was observed during the initial borane complexation step of these reactions. The scope and type of electrophile that can activate dihydrogen in the carbene driven hydrogen storage system is under expansion in order to better manage weight and reactivity in future systems. Recent work has expanded to include (carbonyl)tungsten phosphinidenoids, and phosphonium cations.

Conclusions and Future Directions

We have made substantial progress in the development of new chemistries and computational approaches to meet DOE needs for chemical hydrogen storage. We have developed and used highly accurate computational approaches to design new storage systems, predict new release mechanisms, and design efficient new regeneration mechanisms. We have provided critical data to the process simulations.

A new borane transfer process has been developed which facilitates transfer of a BH_3 unit from sodium borohydride to a variety of amines (including ammonia). A novel hydrogen activation process has been developed which showed that Lewis acid-base pairs need not be “frustrated” in their reactivity towards activating H_2 .

Our experimental chemistry goals include:

- Continue development of a new route to synthesis of AB for first fill.
- The scope and utility of the novel hydrogen activation especially for regeneration is being further investigated. Experiments with a partner in Bonn, Germany will allow for the study of the reaction in a low temperature autoclave.
- Improve kinetics for release and regeneration of H_2 in amino(*Imidazo*)-boranes. Expand to include 1,2,4-triazoles and tetrazole. In the next period, obtain stable azole-borane adducts by starting from the more basic azolides (azole-anions).

Our computational chemistry goals include:

- Continue to support overall center efforts in H_2 release, regeneration of spent fuel, and new concepts including alternative inorganic and organic compounds and mechanisms. We will use DFT benchmarked by accurate MO theory methods to calculate thermodynamics and kinetics and to develop reaction mechanisms and properties for use in process design simulations as well as overall process efficiencies. We will continue to test the prediction of new molecular properties against available experimental data and improve parameterization schemes.
- Use computational approaches to design new catalysts including acid/base catalysts (Lewis acidities, hydride affinities, proton affinities) and transition metal catalysts with specific focus on release and regeneration of spent fuel mechanisms. We will continue our work in the prediction of Lewis acidities with the PNNL as we have the most extensive set of accurate Lewis acidities available for boron compounds.
- Predict thermodynamics and kinetics for regeneration mechanisms. Predict energetics and rates of key steps (examples: digestion, reduction, etc.) to optimize experimental approach.
- Predict thermodynamics for new AB chemistries including new metal/main group BNH compounds ($\text{E}(\text{NH}_2\text{BH}_3)_m$ for activation and AB polymers from anionic polymerization.
- Continue studies of CBNH_x mechanisms to determine underlying physical principles.
- Predict spectroscopic properties (nuclear magnetic resonance, infrared/Raman, ultraviolet-visible) for use in analyzing experimental data.

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20. D.A. Dixon, "Recent UA Computational Work for the DOE Center of Excellence in Chemical Hydrogen Storage," Invited Presentation to the DOE Center of Excellence in Metal Hydrides Meeting, Dec. 18, 2008, California Institute of Technology, Pasadena, CA.
21. D.A. Dixon, invited presentation, "Prediction of Reliable Bond Energies and Molecular Properties for Fluorinated Compounds," 19th Winter Fluorine Conference, St. Petersburg Beach, FL, Jan. 2009.
22. D.A. Dixon, plenary lecture, "Prediction of Reliable Heats of Formation and Bond Dissociation Energies," 49th Sanibel Symposium, Feb. 2009, St. Simons Island, Georgia.
23. D.A. Dixon, Invited lecture, "Computational chemistry for catalysis, hydrogen storage, and the stratosphere," Mississippi State University, March, 2009, Starkville, MS.
24. D.A. Dixon, "Computational Chemistry Support for the DOE CoE in Chemical Hydrogen Storage," Tech Team Review, March 2009, Detroit, MI.
25. A.J. Arduengo, III, "Poly(imidazol(in)ylidene) und Chelatisierende Imidazol(in)ylidene: Entwicklungen aus der Carben-Chemie," Organisch-Chemisches-Kolloquium International, Marburg, Germany (December, 2008).
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IV.B.1f Low-Cost Precursors to Novel Hydrogen Storage Materials

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Contract Number: DE-FC36-05GO15053

Subcontractors:

- Battelle Energy Alliance, LLC (BEA), Idaho, ID
- Innochem, Inc., Boxford, MA
- Electrolytica, Inc., Amherst, NY

Project Start Date: March 1, 2005
Project End Date: March 31, 2010

Objectives

- Overall: Develop and advance novel hydrogen storage materials to meet DOE 2010 targets and that have the potential to meet 2015 targets.
- Phase 1 - Define/evaluate novel chemistries and processes for producing chemical hydrides:
 - Emphasize low-cost routes to regenerate sodium borohydride (NaBH_4) from spent borate fuel.
- Phase 2 - Identify cost and energy efficient pathways to first-fill and regeneration for ammonia borane (AB) and other borane materials:
 - Continue experimentation leading to selection of single pathway for low-cost NaBH_4 and further AB process technology development.
 - Guide selection of a top AB regeneration scheme for experimental studies on most promising alternatives.

Technical Barriers

This project addresses the following technical barriers from the Storage section (3.3) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (B) System Cost
- (R) Regeneration Processes (Cost, Energy Efficiency, Environmental Impacts)

Technical Targets

- **Fuel Cost – Regenerated AB.** Table 1 shows progress against meeting the DOE 2010 and 2015 targets for fuel cost using the AB regeneration scheme developed by Los Alamos National Laboratory (LANL) (thiol-based digestion followed by reduction using tin hydride compounds). Capital recovery and utilities account for 75% of the regeneration cost and are dominated by high mass flow and separation requirements. Several opportunities to reduce cost and energy usage in the LANL process, and thereby lower the fuel cost, have been identified. Additionally, LANL has recently announced a new, much simplified regeneration scheme. Cost estimation for the new scheme is in progress.

TABLE 1. Progress Towards Meeting Technical Targets for Ammonia Borane

Characteristic	Units	2010/2015 Targets	Regenerated AB Status
Fuel Cost	\$/gge at pump	2 - 3	7 – 8*

* Based on 250 and 100 mt/day (TPD) H_2 equivalent AB production plants

- **System Storage Cost – First-Fill AB.** The cost for first-fill AB, synthesized using the route developed by Purdue University was estimated to be \$9/kg AB. This assumes \$5/kg NaBH_4 and 10,000 metric tonne per annum (MTA) AB production.

Figure 1 relates AB cost to H_2 cost and shows that, using the above assumptions, it may be possible to meet the 2010 system storage cost target. Sodium borohydride is a dominant component of first-fill AB cost, however, and underscores the importance of developing a lower cost NaBH_4 route, especially when the 2015 target is considered.

FIGURE 1. First-Fill AB Cost: Impact on Storage System Cost

Accomplishments

- The cost to produce first-fill AB, assuming \$5/kg NaBH_4 starting material and using the Purdue ammonium formate metathesis route, was estimated at \$9/kg AB. This may enable the 2010 target for system storage cost to be met. Sodium borohydride accounts for 75% of the cost to produce make AB, hence, low-cost NaBH_4 is critical to meeting the 2015 system storage cost target.
- Alane reduction of borate to borohydride was shown in the laboratory to afford high purities (99+%) and yields (97%). The high material balance closures and lack of intractable by-products point to a recyclable process for lower cost NaBH_4 for first-fill AB.
- The baseline cost for regenerated AB using the thiol-based route developed by LANL was estimated at \$7–8/kg H_2 , compared with the DOE 2010/2015 target of \$2–3/gge. Capital recovery and utilities are dominant components of the cost. Several opportunities to lower processing and separation costs have been identified.

Introduction

This project focuses on identifying and developing viable hydrogen storage technologies using chemical hydrides that have the potential to achieve DOE 2010 and 2015 performance targets for transportation applications. In collaboration with the other Center participants, efforts are directed towards defining and evaluating novel chemistries and processes for producing chemical hydrides. In Phase 1, emphasis was on NaBH_4 , initially a strong candidate for hydrogen storage because of its hydrogen storage capacity, chemistry, safety, and functionality.

The ability to produce low-cost NaBH_4 in an energy-efficient, cost-effective, and environmentally sound

manner is critical to the commercial success of virtually any boron-based fuel, including AB. In Phase 2, research continues towards identifying and developing a single low-cost NaBH_4 synthetic route for cost-efficient AB first-fill, and conducting baseline cost estimates for first-fill and regenerated AB using a variety of synthetic routes.

Approach

This project utilizes an engineering-guided research and development approach which involves the rapid down-selection of a large number of options (chemical pathways) to a smaller, more manageable number. The down-selection is based on evaluation against a set of fast-fail metrics and can occur before experimentation is initiated. This helps focus efforts and resources on the options with the highest technical and commercial probability of success. A detailed engineering analysis methodology has been established for conducting cost and energy-efficiency calculations. The methodology utilizes a number of inputs and tools (Aspen IPE™, FCHTool, and H2A).

Results

Previously, we reported on the identification of two leading pathways to convert borate to borohydride—metal reduction and carbothermal reduction—based on a comprehensive review of possible pathways, scoring against established metrics, and initial laboratory feasibility studies. Both routes were shown to offer a significant cost reduction and metal usage compared to the current, commercial Schlesinger process, which utilizes four moles of sodium metal to produce one mole of NaBH_4 .

With the September 2007 No-Go decision for NaBH_4 as an on-board hydrogen storage medium, focus was shifted to AB for on-board hydrogen storage and delivery. In Phase 2, the primary objective of this work is to identify cost and energy efficient routes for first-fill AB (storage system cost) and for regenerated AB (fuel cost). Since NaBH_4 is a starting material for AB and other boron-based fuels, including several materials currently under consideration by the Metal Hydride Center of Excellence, these materials will require low-cost NaBH_4 for initial system fill.

First-Fill AB - Baseline Cost Estimate. In recent years, several attractive routes affording high AB yields have been reported. Purdue and the Pacific Northwest National Laboratory (PNNL) have pursued metathesis routes [1,2]:

Ohio State researchers have demonstrated AB formation via base displacement of borane complexes with ammonia [3]:

Initial efforts focused on the Purdue chemistry, specifically the ammonium formate/dioxane route, due to more facile separation of sodium formate by-products from unreacted ammonium formate (compared with the corresponding sulfate salts). A conceptual process flowsheet was developed for this process, and engineering analysis methodology was applied to arrive at an overall cost of \$9/kg AB for a 10,000 MTA sized AB plant. Sodium borohydride pricing of \$5/kg was used as an initial estimate for first-fill AB scales. These results were reviewed and validated by TIAx.

It can be seen from Figure 2 that approximately 80% of the cost to produce AB by this route is due to raw materials, and of this, NaBH_4 at \$5/kg accounts for 95% for an overall cost component of 75%.

Hydrogen storage media costs based on \$9/kg AB are approximately \$55/kg H_2 (Figure 1). When considered as part of the overall storage system cost, it is clear that NaBH_4 pricing significantly lower than \$5/kg is needed if the 2015 target is to be met.

Low-Cost NaBH_4 for First-Fill AB. Metal reduction of borate can proceed via a one-step or two-step process as shown below. Recycle of the resulting metal oxide back to the metal in a cost-effective manner is also required.

In Fiscal Year 2009, laboratory studies were re-initiated with the objective of validating prior reactive milling results for, and determining the scalability of, the two-step metal reduction process. The two-step process via metal hydride intermediate offers the advantage of higher yields and lower reaction severities. Much of the work has focused on aluminum as the reductant (ligand-stabilized alanes) in commercially available laboratory-scale ball mills.

Table 2 shows the effect of various chemistry parameters on NaBH_4 yield. To date, essentially complete mass balance closure has been obtained. Sodium borohydride in high purity (99%) has been isolated, with good yields (97%). Essentially all of the

FIGURE 2. First-Fill AB Cost Breakdown – Purdue Scheme

TABLE 2. Effect of Reaction Parameters on NaBH_4 Yield

Chemistry (Ball Milling)	Borate Source	NaBO_2 : 89% NaBH_4 , 5% BH $\text{Na}_2\text{B}_4\text{O}_7 + \text{NaX}$: 62% NaBH_4
	Alane Adduct	L1: 89% NaBH_4 , 5% BH L2: 1% NaBH_4 , 29% BH L3: 2% NaBH_4
	Stoichiometry	1.1 eq. $\text{AlH}_3\text{-L}$: 60% NaBH_4 , 1% BH 2.0 eq. $\text{AlH}_3\text{-L}$: 77% NaBH_4 , 1% BH
Alternative Approaches	(Slurry-Based Systems)	Borate + $\text{AlH}_3\text{-L} \rightarrow$ 29% NaBH_4 + 60% BH 89% boron conversion

Results based on ^{11}B nuclear magnetic resonance (NMR) analysis; BH = borane intermediate

ligand can be recovered, and no intractable by-products have been identified. This points to a recyclable process (Figure 3).

In addition to the parameters shown in Table 2, the effects of a variety of milling parameters (i.e., reaction time, ball size, ball-to-powder ratio) have also been investigated. Discrete-element modeling is being used to provide a fundamental understanding of mill motions and energy distribution of particle collisions. Initial results have provided insight into mill operation, scaleup and design, and are helping to guide laboratory studies to identify a scalable process.

FIGURE 3. Chemical Pathway for Aluminum Reduction of Borate to Borohydride

Carbothermal borate reduction is characterized by the following equation:

Methane (instead of metal) is used as the reductant, thereby eliminating the need for metal oxide recycle and associated cost and energy requirements. High temperatures (generally >1,200°C) are required before these reactions become thermodynamically favorable.

Carbothermal studies utilizing plasma techniques have been undertaken by sub-contractor Idaho National Laboratory (INL). In FY 2009, work was commenced with the objective of reproducing 2007 INL studies which gave 40–50% NaBH₄ yield (based on ¹¹B NMR analysis) in a one-step plasma reactor. Additional goals were to gain an understanding of intermediates and byproducts formation and their required separation, reaction quench and heat integration needs, and ultimately identify scaleup options for commercial high temperature operations.

At the time of this reporting, it has not been possible to reproduce past positive results for NaBH₄ using the plasma carbothermal process. However, some yet to be identified water-reactive species (possibly boranes, Na, or NaH) have been produced. Assistance is being provided to INL in troubleshooting various equipment and analytical issues, guiding the experimental studies, and in determining an overall mass and boron balances for the system.

AB Regen Baseline Cost Estimate. Center partners LANL, University of Pennsylvania, and PNNL have each developed AB regeneration schemes that have been demonstrated to varying extents. Engineering analysis of the proposed schemes is being provided to the partners to

AB Production, TPD H ₂ equivalent	100	250
Baseline AB Regen Plant Cost, \$/kg H ₂	7.9	7.0
Total Investment, \$M	520	1000
Capital	460	850
First Fill Chemicals (dominated by tin)	60	150

FIGURE 4. Cost Breakdown for LANL AB Regeneration Scheme

help guide the selection of the most energy-efficient and cost-effective route. LANL's route, based on thiol digestion of the spent fuel followed by reduction to AB using tin hydride compounds, was selected first for analysis.

A conceptual process flowsheet was developed for the LANL process and the same engineering analysis methodology applied for first-fill AB cost estimation was applied. Assuming 225,000 MTA AB production (equivalent to 100 TPD H₂ @ 90% on-stream) and 2.5 mol H₂ release per mol AB, a baseline cost estimate of approximately \$8/kg H₂ was calculated. A cost estimate for 250 TPD H₂ equivalent conducted as a sensitivity case resulted in \$7/kg H₂. These results were also validated by TIAX.

Cost breakdown for the LANL AB regeneration scheme is shown in Figure 4. Capital recovery and utilities account for 75% of the cost to regenerate AB. This is dominated primarily by high mass flows (dilute solutions, heavy tin reductant) and separation requirements. Several opportunities have been identified to lower the cost and energy requirements for this

process (i.e., minimizing refrigeration, alternatives to distillation, reducing separation requirements). These may enable AB regen costs to approach the DOE 2010/2015 fuel cost target of \$2–3/gge.

Additionally, LANL has recently reported a much simplified AB regen route which promises to be more cost-effective and energy-efficient than the thiol-based route. A baseline cost estimate for this approach will be conducted.

Conclusions and Future Directions

Conclusions

- Low-cost NaBH_4 as a starting material for first-fill AB is critical to meeting DOE system storage cost targets. At \$5/kg NaBH_4 , the baseline cost estimate for first-fill AB is \$9/kg AB (10,000 MTA sized AB plant), which may enable the 2010 target to be met, and significant further reduction in NaBH_4 cost will be necessary to be able to meet the 2015 system storage cost target.
- A laboratory-scale process has been demonstrated for reduction of borate to borohydride using alane as the metal reductant. The process affords high yields and high purity NaBH_4 and appears to be recyclable. Demonstration of the scalability of this process is a key technical challenge. Other, more scalable routes are also being investigated.
- At \$7–8/kg H_2 , the baseline cost estimate for AB regenerated using the LANL thiol-based route exceeds the 2010-/2015 target of \$2–3/gge. However, several options to reduce the cost have been identified and are being investigated, as is a much simplified regeneration route (also developed by LANL).

Future Directions

- First-fill AB: Conduct baseline cost estimate for PNNL and Shore schemes and refine cost estimates with updated NaBH_4 cost.
- Low-cost NaBH_4 for first-fill AB: Progress research and development to identify low-cost, scalable process.
 - Metal reduction: demonstrate and select best scalable process.
 - Carbothermal: progress experimental project to validate prior positive results, develop conceptual process and cost.

- Select single top pathway and further develop process, confirm scalability, update flowsheets and economics.

- Regenerated AB
 - Investigate options to lower cost of LANL regen scheme (reduce mass flow, separation requirements).
 - Conduct baseline cost estimate for new, simplified LANL regen route.

Patents

1. “Process for Production of a Borohydride Compound,” A.A. Chin, P. Jain, S.W. Linehan, F.J. Lipiecki, S.G. Maroldo, S.J. November, and J.H. Yamamoto, non-provisional patent application, filed February 23, 2009.

FY 2009 Publications/Presentations

1. “Ammonia Borane 1st Fill and Regeneration Assessments,” A.A. Chin, F. Lipiecki, S. Linehan, N. Allen, R. Butterick, L. Klawiter, S. Nadeau, S. November, FreedomCar Tech Team Meeting, March 19, 2009, Detroit, MI.
2. “Low-Cost Precursors to Novel Hydrogen Storage Materials,” S. Linehan, N. Allen, R. Butterick, A. Chin, L. Klawiter, F. Lipiecki, S. Nadeau, S. November, DOE Annual Merit Review, Washington, D.C., May 21, 2009.

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IV.B.1g Ammonia Borane Regeneration and Market Analysis of Hydrogen Storage Materials

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Contract Number: DE-FG36-08GO18140

Project Start Date: October 1, 2008
Project End Date: September 30, 2010

Objectives

- Synthesize target borate ester expected to have enhanced hydride affinity for use in demonstrating a practical ammonia borane regeneration cycle.
- Supply selected borate esters to project collaborators at the Pacific Northwest National Laboratory (PNNL).
- Assess U.S. and global borate resources and reserves available for large-scale implementation of ammonia borane as a transportation fuel.
- Estimate U.S. and global borate reserves available in 2050, adjusted for consumption by competing industrial uses.

Technical Barriers

This project addresses the following technical barriers from the Storage section (3.3) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (B) System Cost
- (C) Efficiency
- (K) System Life Cycle Assessments
- (R) Regeneration Processes

Technical Targets

Regeneration There is a need to maximize efficiency of off-board regeneration of ammonia borane:

- Recyclable thermodynamically favorable intermediates are required.
- We are collaborating with PNNL and other Chemical Hydrogen Storage Center of Excellence (CHSCoE) partners to maximize efficiency of spent fuel regeneration.
- Our work involves tuning the chemistry of borate esters as hydride acceptors in PNNL's cycle.

Boron Resources An understanding of the global supplies of boron ore resources is required for hydrogen storage:

- A key objective is to develop a better understanding of global supplies of boron ore reserves required for hydrogen storage.
- In addition to boron, a resource model developed as part of this work will be applicable to other materials of interest for hydrogen storage, e.g., Li, Mg.

Accomplishments

- Prepared a series of target borate ester compounds and supplied these to collaborators at PNNL for testing as hydride acceptors in a practical ammonia borane regeneration cycle.
- Completed assessment of global borate reserves, including estimated reserve base in 2050 adjusted for consumption by existing industrial applications.

Introduction

A major emphasis of the CHSCoE is the regeneration of ammonia borane (AB) spent fuel. This has created needs in areas in which U.S. Borax Inc. (USB) has strong capabilities. USB is collaborating with the CHSCoE to assist in solving important problems relating to the use and regeneration of ammonia borane as an off-board reversible hydrogen storage material, with activities in the following areas critical to key goals: 1) synthesis of borate esters related to AB fuel regeneration intermediates, and 2) analysis of boron resources and impacts on supplier and end-use industries. As strategies for AB fuel regeneration have progressed, more attention has focused on borate ester

chemistry. Given its considerable experience with the synthesis and process development of borate esters, USB is collaborating with members of the CHSCoE to identify a set of borate esters that can be prepared from digested AB spent fuel (BNH_x), and can be converted back to AB in an efficient process.

In addition, the impacts on boron resources associated with the initial fill requirements of a large AB-fueled automotive fleet require further analysis. USB is undertaking a study to address frequently asked questions regarding the adequacy of key boron resources, production capacities needed to meet a steeply rising demand curve followed by a return to baseline, and impacts upon prices and competing end-uses.

Approach

Activity 1. Regeneration of AB Spent Fuel

- PNNL's proposed regen cycle has high theoretical efficiency.
- Use alcohols for digestion of spent AB leads to borate ester intermediates.
- Tuning the properties of aryl borates esters will lead to thermodynamically favorable regen intermediates and validate computations.
- AB regeneration pathway requires spent fuel digestion intermediate having sufficient hydride affinity for reduction by metal hydride.
- USB is undertaking synthesis of a large set of borate esters of several types to be supplied to PNNL for experimental validation of theory and regen process.
- Approach will impact likelihood of success of PNNL's regen system and validate theory.

Activity 2. Establish Global Reserve Estimates

- Review and analyze publicly available information sources to quantify borate resources.
- Other published numbers have poorly attributed data sources.
- Our work is aimed at establishing most reliable publicly available reserves data.
- Anticipated consumption of reserves from competing uses through projected initial fill timeframe (2009 → 2050) should be included in estimates.

Results

Activity 1. Regeneration of AB Spent Fuel

A major activity of this project is the preparation of borate esters that can be reduced to borane as part

FIGURE 1. Halogenated Orthoborate Esters

of a practical regeneration cycle, returning BNH_x (spent fuel) to AB fuel. This requires esters that have enhanced hydride affinities. Calculations done at PNNL and elsewhere indicate that phenolic esters possessing electrophilic substituents may have suitable hydride affinities. In order to validate these calculations, we have set out to prepare a series of orthoborate esters of the type shown in Figure 1, where X is fluorine or chlorine and $n = 1-5$.

At this point we have evaluated various laboratory methods that can be applied to the systematic synthesis of a complete series of borate esters that are substantially free of hydroxyl group-containing contaminants (R-OH , $=\text{B-OH}$, H_2O). While still experimenting with these methods, we have prepared a number of target borate esters, which were supplied to our collaborators at PNNL for nuclear magnetic resonance (NMR) spectral analysis and further testing in connection with ammonia borane regeneration.

- Another approach to controlling the hydride affinities of borate esters involves the use of chelated esters. To this end, we have prepared several borate esters of the type shown in Equation 1, where X is chlorine in our initial experiments. In each of the chlorine-containing ligands, the

halogen substituents were at ortho positions relative to the phenolic $-\text{OH}$ groups. Because the presence of the imine functionality is undesirable in hydride transfer reactions, we have reduced these imine precursors to amines and also formed borate ester from these reduced ligands. We accomplished these objectives in a one-step reaction using sodium borohydride as both reductant and boron source, as shown in Equation 1. The products were characterized by gas chromatograph mass spectroscopy and NMR spectroscopy. Borate ester compounds prepared in our laboratory and supplied to PNNL collaborators so far during 2009 include those listed in Table 1.

TABLE 1. Borate Ester Compounds Prepared and Supplied to PNNL in 2009

Chlorophenylborate esters	
Tri(2-chlorophenyl)orthoborate	$B(O-o\text{-ClC}_6\text{H}_4)_3$
Tri(3-chlorophenyl)orthoborate	$B(O-m\text{-ClC}_6\text{H}_4)_3$
Tri(4-chlorophenyl)orthoborate	$B(O-p\text{-ClC}_6\text{H}_4)_3$
Tri(2,4-dichlorophenyl)orthoborate	$B(O-2,4\text{-Cl}_2\text{C}_6\text{H}_3)_3$
Tri(2,6-dichlorophenyl)orthoborate	$B(O-2,6\text{-Cl}_2\text{C}_6\text{H}_3)_3$
Tri(3,4-dichlorophenyl)orthoborate	$B(O-3,4\text{-Cl}_2\text{C}_6\text{H}_3)_3$
Tri(3,5-dichlorophenyl)orthoborate	$B(O-3,5\text{-Cl}_2\text{C}_6\text{H}_3)_3$
Tri(2,4,6-trichlorophenyl)orthoborate	$B(O-2,4,6\text{-Cl}_3\text{C}_6\text{H}_2)_3$
Fluorophenylborate esters	
Tri(2-fluorophenyl)orthoborate	$B(O-o\text{-FC}_6\text{H}_4)_3$
Tri(3-fluorophenyl)orthoborate	$B(O-m\text{-FC}_6\text{H}_4)_3$
Tri(4-fluorophenyl)orthoborate	$B(O-p\text{-FC}_6\text{H}_4)_3$
Tri(3,4-difluorophenyl)orthoborate	$B(O-3,4\text{-F}_2\text{C}_6\text{H}_3)_3$
Tri(3,5-difluorophenyl)orthoborate	$B(O-3,5\text{-F}_2\text{C}_6\text{H}_3)_3$
Tri(3,4,5-trifluorophenyl)orthoborate	$B(O-3,4,5\text{-F}_3\text{C}_6\text{H}_2)_3$
Mixed halophenylborate esters	
Tri(2-fluoro-4-chlorophenyl)orthoborate	$B(O-2-F-4\text{-Cl-C}_6\text{H}_3)_3$
Tri(2-fluoro-4-bromophenyl)orthoborate	$B(O-2-F-4\text{-Br-C}_6\text{H}_3)_3$

Activity 2. Establish Global Reserve Estimates

A second major activity of this project is the analysis of the impacts on boron resources associated with the initial fill requirements of a boron-based fuel for a large automotive fleet. Initially, this requires an assessment of world boron resources in terms of known borate minerals reserves. This involves analysis and reconciliation of publicly available information on borate reserves in various parts of the world. To date, we have compiled and analyzed key public sources of information and refined the combined borate resource estimates. These estimates were projected out to 2050 using estimates of boron demands from other competing industrial applications, to produce an adjusted assessment of boron resources over the time frame relevant to hydrogen fuel cell vehicle (FCV) deployment. These data were then compared with estimates of boron requirements for hydrogen storage in FCVs.

The first priority of our work was to establish the most credible estimates of boron reserves. It can be noted that publicly available reports and discussions of borate reserves differ markedly. For example, the U.S. Geological Survey figures are the lowest in the literature [1]. Furthermore, the variance is greatest for the two nations with the largest reserves, the United States and Turkey. We determined that other sources of information are more realistic [2,3]. This analysis, based upon publicly available data sources deemed to be reliable,

indicates that available boron from known reserves exceeds 1 billion metric tonnes of boric oxide (B_2O_3).

The model we used for boron demand resulting from FCV deployment employed the assumptions listed in Table 2. Boron demand associated with automotive use of ammonia borane hydrogen storage material was based on the known chemistry of the AB storage system and the number of FCVs to be deployed, as projected in

TABLE 2. Assumptions Used in Boron Demand Model

No. FCVs deployed in USA by 2050	60 million
No. FCVs deployed worldwide by 2050	360 million
Miles per kg H_2	57.5*
Miles range per tank	400
Miles per year per FCV	12,000*
Months supply in infrastructure	1
% H_2 stored in ammonia borane	15
% Recycle	100 (insignificant losses)
	* from H2A model

the Department of Energy publication, *Analysis of the Transition to Hydrogen Fuel Cell Vehicles & Potential Hydrogen Energy Infrastructure Requirements* (ORNL/TM-2008/30), and the VISION model. Using these methods, we calculated the cumulative boron demand associated 360 million FCVs deployed by 2050 as 60 million metric tonnes B_2O_3 .

Our assessment of global borate resources, summarized in Figure 2, indicates that more than 1 billion B_2O_3 tonnes are available from known borate reserves. Figure 2 also shows the cumulative amounts of B_2O_3 estimated to be required for both a U.S. and a global fleet of FCVs fueled with ammonia borane.

FIGURE 2. Estimated global borate resources showing the cumulative amounts of B_2O_3 estimated to be required for both a U.S. and a global fleet of FCVs fueled with ammonia borane.

FIGURE 3. Comparison of boron reserves in the U.S., showing estimated depletion by existing non-hydrogen storage applications, with the projected demand from a U.S. fleet of FCVs.

Figure 3 shows the known U.S. borate reserves, with a projection of how these reserves might be depleted over time by the demands of existing non-hydrogen storage applications, compared with the requirements of a U.S. fleet of 360 million FCVs, 60 million B_2O_3 tonnes. The conclusions drawn from these data is that, even when other competing applications are factored in, there is sufficient borate reserves within the United States to satisfy the B_2O_3 requirements for initial fill of a U.S. FCV fleet.

Our conclusion from this initial work is that global borate ore reserves are sufficient for hydrogen storage needs, as well as the other industrial demands projected over the relevant time period. In addition, we further conclude that borate reserves within the U.S. are sufficient to supply a U.S. fleet of 360 million FCVs. Further refinements to these estimates, and sensitivity analyses, will be done during subsequent performance periods of this project, but these refinements are not expected to alter our basic conclusion that sufficient borate reserves are available for automotive hydrogen storage needs.

Conclusions and Future Directions

Future Directions

- Further refinement of boron global reserve data.
- Analysis of important questions regarding industry impacts of hydrogen storage technologies and market parameters, including:
 - Impacts on competing uses.
 - Impacts on borate prices.
- Prepare larger set of borate esters of several categories for regen studies at PNNL.
- Conduct spent fuel digestion studies.
- Regen cycle validation in collaboration with PNNL.

FY 2009 Publications/Presentations

1. Two quarterly reports were submitted to the DOE.
2. This project was presented for peer review at the DOE Annual Review Meeting in Washington, D.C. in May, 2009.

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2. *Borates: A Handbook of Deposits, Processing, Properties, and Use*, D.E Garret, Academic Press, San Diego, CA, 1998, p 442.
3. *The Economics of Boron – 11th Edition*, Roskill Information Services: London, England, 2006, Chapters 1 & 2.

IV.B.1h Hydrogen Storage by Novel CBN Heterocycle Materials

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Project Start Date: September 1, 2008
Project End Date: August 31, 2011

Objectives

The objective of this project is to develop novel boron-nitrogen heterocycles as liquid-phase hydrogen storage materials with storage capacities and thermodynamic properties that have the potential to lead to rechargeable systems capable of meeting DOE targets. We seek to:

- Develop new materials that:
 - (a) exhibit appropriate enthalpy of H₂ desorption
 - (b) are liquids at operating temperatures
 - (c) possess high H₂ storage capacities
- Identify catalysts that will release hydrogen from these materials at temperatures <200°C.
- Develop conditions that will readily recharge the spent fuel.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) System Weight and Volume
- (C) Efficiency
- (R) Regeneration Process

Technical Targets

This project is developing new liquid phase materials for hydrogen storage that can be readily regenerated. Insights gained from these studies will be applied toward the design and synthesis of hydrogen storage materials that meet the following DOE 2010 hydrogen storage targets:

- System Gravimetric Density = 4.5 wt%
- System Volumetric Density = 28 g/L

Accomplishments

- Identified three materials with favorable thermodynamics and down-selected four potential materials with the help of computation.
- Synthesized a complete set of model heterocycle materials with different degree of hydrogen content. This will allow the determination of the thermodynamics of hydrogen desorption and absorption via experimental measurement and thus provide a feedback loop to the calculated values.
- Demonstrated that the spent fuel readily absorbs two equivalents of H₂ under mild conditions.

Introduction

Hydrogen storage is a vital component in the development of a hydrogen-based energy infrastructure. Boron nitrogen containing compounds, e.g., ammonia-borane (H₃N-BH₃ or AB), have attracted much attention as chemical H₂ storage materials because of their high gravimetric hydrogen densities and fast kinetics of H₂ release [1]. This project is developing CBN hydrogen storage materials (i.e., heterocycles containing carbon, boron, and nitrogen) that are liquid-phase and have the potential to be reversibly regenerated using molecular hydrogen. A liquid phase, hydrogen storage system that can be regenerated using molecular hydrogen is highly desired for many reasons, including versatility, lower cost and improved efficiency, and durability. Such a storage material will allow on-board hydrogen storage. It can also be applied as an off-board energy carrier for vehicle and stationary applications that takes advantage of the existing liquid fuels infrastructure.

Approach

In order to accomplish reversibility, neutrality in free energy of the hydrogen release process (i.e., ΔG ~0 kcal/mol) at the operating temperature is

pivotal. The dehydrogenation of AB is exergonic by -13 kcal/mol at 298 K (Eq. 1). In contrast to AB, the dehydrogenation of its isoelectronic organic counterpart, ethane ($\text{CH}_3\text{-CH}_3$), is endergonic by $+25$ kcal/mol (Eq. 2). The coupling of endothermic dehydrogenation from carbon-carbon with exothermic dehydrogenation from BN in a cyclic six-membered framework could lead to a reversible H_2 storage system. Indeed, high-level computational analysis indicates that the release of H_2 from CBN heterocycles (denoted as “1” in Eqs. 1-3) has favorable overall thermodynamics conducive to reversibility, (e.g., see Eq. 3) [2]. The potential for reversible hydrogen release/uptake and the relatively high gravimetric hydrogen density of CBN heterocycle materials (e.g. 7.1 wt% for 1) render their preparation and development an important goal. In a collaborative effort with the Chemical Hydrogen Storage Center of Excellence (CHSCoE), this project is investigating several CBN heterocycle materials for H_2 storage applications using a synergistic theoretical and experimental approach. Synthesis will be a crucial component of this project given the relatively unexplored nature of these CBN heterocycles.

Results

Thermodynamic Analysis of CBN Heterocycle Materials

We used theory to guide our initial target selection for synthesis. Scheme 1 illustrates the calculated thermodynamic data for H_2 desorption for the seven proposed CBN materials. Theory predicts that Materials (1), (3), and (7) have the potential for reversibility ($\Delta\text{G} \sim 0$ kcal/mol) [2]. Detailed thermodynamic analyses, including consideration of multiple pathways for H_2 release have been calculated for Materials (1)-(3). Current efforts are geared toward completing the detailed pathway analysis for all the proposed materials. With the help of theory we conclude that our synthetic efforts should be initially directed toward Materials (1), (3), and (7).

SCHEME 1. Calculated Thermodynamic Properties of CBN Heterocycles

Synthesis of Model CBN Heterocycle Materials

The hydrogen release from heterocycle 1 can potentially involve partially spent-fuel intermediates 3-6 (Scheme 2, top). Synthetic access to all compounds on the pathway from the fully charged material 1 to the discharged fuel 2 will be essential to understand and improve the H_2 release and uptake properties of this particular storage system. Heterocycle 1 has been reported but it has not been isolated [3]. To the best of our knowledge, intermediates 3-6 are still elusive. We recently successfully prepared the fully discharged material, 1,2-dihydro-1,2-azaborine 2 [4]. One challenge we encountered in the synthesis of 2 is the removal of a protecting group from nitrogen to introduce the N-H bond. To avoid the synthetically challenging deprotection step, we pursued the preparation of *N*-protected derivatives 2'-6' ($\text{R} = t\text{-Bu}$, Scheme 2, bottom) as models for 2-6. High-level calculations show that the thermodynamic properties of CBN Material (1) do not change significantly when the nitrogen is protected with a *t*-Bu group (Scheme 2) [2].

SCHEME 2. CBN Heterocycle Material (1) and its Model System

Scheme 3 (top) illustrates the synthesis of **2'**-**6'**. We previously reported the preparation of heterocycle **7** [5], which reacts with LiHBEt_3 to furnish one of the desired intermediates **5'**. Compound **5'** subsequently serves as a common precursor to **2'** and **3'** under catalytic dehydrogenation and hydrogenation conditions, respectively. Treatment of **7** with KNPh_2 produces compound **8**, which isomerizes to the *N*-vinyl isomer **9** in the presence of a ruthenium catalyst. Displacement of the diphenylamino group with LiAlH_4 generates isomer **4'**. The synthesis of **6'** commences with the condensation of homoallylic amine **10** with the in situ generated vinylboron dichloride to yield **11**. Subsequent ring-closing metathesis of **11** using Grubbs 1st generation catalyst followed by nucleophilic substitution of the B-Cl bond with LiHBEt_3 generates CBN heterocycle **6'**. All these syntheses are preliminary, and the yields have not been optimized. Compounds **2'**-**6'** are all liquids with melting points below -30°C .

We chose to prepare **1''** as a synthetic model for **1**. Scheme 3 (bottom) illustrates our synthetic pathway to **1''**, which was adapted and optimized from the route reported by Vedejs et al. [3]. Treatment of homoallylic amine **12** with $\text{BH}_3\cdot\text{THF}$ furnished the amine-borane complex **13** in high yield. Subsequent reaction of **13** with a catalytic amount of elemental bromine resulted in a directed intramolecular hydroboration to yield the desired **1''**. Thus, we have accomplished the synthesis of representative model compounds on the pathway from

the fully charged material **1** to the discharged fuel **2**. Compounds **2'**-**6'** have been delivered to our CHSCoE partners at University of Washington for catalytic H_2 absorption/desorption studies. The synthesis of compound **1''** will be scaled up and delivered to our center partners as well.

Development of Conditions/Catalysts that will Recharge the Spent Fuel

With CBN heterocycles **2'**-**6'** in hand (see Scheme 2), we began to investigate the regeneration of spent-fuel material **2'** using molecular H_2 . Our initial attempt met with failure. Treatment of **2'** in the presence of Pd black as a catalyst under 35 psi H_2 pressure at 80°C in deuterated benzene did not result in any hydrogen uptake (Eq. 4). However, upon further investigation, we subsequently determined that the choice of the catalyst is crucial for reactivity. Under identical conditions as illustrated in Eq. 4, the spent-fuel material **2'** readily takes up two equivalents of H_2 to furnish **3'** when Pd/C is used as a catalyst instead of Pd black (Eq. 5). The reaction solvent benzene- d_6 is not hydrogenated under the reaction conditions. Given that compound **2'** is an aromatic molecule – **2'** is isoelectronic and isostructural with benzene – Eq. 5 suggests that the activation barrier for hydrogen uptake is substantially lower for CBN heterocycle material **2'** than for the corresponding aromatic carbocycles.

SCHEME 3. Synthesis of Model Compounds of CBN Material (1)

Conclusions and Future Directions

In summary, we developed a versatile synthetic toolbox that led to the preparation of CBN H_2 storage materials. We determined that 1) model compounds of CBN hydrogen storage Material (1) are low-melting liquids, and 2) regeneration of its spent fuel can be accomplished using molecular H_2 under mild conditions (80°C and 35 psi H_2 pressure for 2 out of 3 possible H_2 equivalents).

In Fiscal Year 2010, we will:

- Optimize our current synthetic toolbox with regard to yields and efficiency.
- Prepare CBN Material (1).
- Prepare CBN heterocycles related to Material (7).
- Determine experimental thermodynamic properties for model CBN heterocycles.
- Continue develop conditions/catalysts for recharging the spent fuel.
- Develop conditions/catalysts for H₂ desorption.

FY 2009 Publications/Presentations

1. “A Hybrid Organic/Inorganic Benzene”; A.J.V. Marwitz, M.H. Matus, L.N. Zakharov, D.A. Dixon, S.-Y. Liu, *Angew. Chem. Int. Ed.* **2009**, 48, 973-977.
2. “1,2-Dihydro-1,2-Azaborine: An Organometallic Benzene”; S.-Y. Liu, *IMEBoron XIII International Boron Conference*, Platja d'Aro, Spain, September 2008.
3. “Hydrogen Storage by Novel CBN Heterocycle Materials”; S.-Y. Liu et al.; poster presented at the *D.O.E. Hydrogen Annual Review*, Washington, D.C., May 2009.
4. “Hydrogen: A Drive to the Future”; Kshitij Parab, Patrick Campbell, Shih-Yuan Liu; poster presented at the *Hydrogen Road Tour '09 Eugene Stop*, Eugene, OR, May 2009.

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IV.B.1i Solutions for Chemical Hydrogen Storage: Dehydrogenation of B-N Bonds

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Contract Number: DE-FC36-05GO15057

Project Start Date: March 1, 2005
Project End Date: February 28, 2010

Objectives

- Identify materials/systems to meet DOE target goals for gravimetric and volumetric densities of H₂:
 - Amineboranes and other boron-nitrogen (BN) compounds have potential for high H₂ storage capacities.
- Develop cost-effective metal catalysts for the dehydrogenation of BN hydrogen storage materials:
 - Focus on cheap widely available non-platinum group metals such as cobalt and iron.
- Optimize catalysts to meet DOE target goals for H₂ discharging rates from BN materials.
- Collaborate with the University of Oregon to develop systems based on novel carbon-boron-nitrogen (CBN) materials:
 - CBN materials have the potential for direct regeneration. Will need to identify and investigate catalysts capable of dehydrogenating both B-N and C-C bonds.

Technical Barriers

This project addresses the following technical barriers from the Storage section (3.3.4.2) of the Hydrogen, Fuel Cells and Infrastructure Technologies

Program Multi-Year Research, Development and Demonstration Plan:

- (A) System Weight and Volume
- (B) System Cost
- (E) Charging/Discharging Rate
- (R) Regeneration Processes

Technical Targets

Amineboranes are promising substances for chemical hydrogen storage, provided that efficient catalysts can be developed to liberate the stored hydrogen rapidly. This project is working to develop cost-effective catalysts for the dehydrogenation of amineboranes. We are also working to develop new mixed CBN materials that have the potential to be directly regenerated. Insights gained from these studies will be applied toward the design of hydrogen storage materials that meet the following DOE 2010 hydrogen storage targets:

Cost: \$4/kWh net

Specific energy: 1.5 kWh/kg

Energy density: 0.9 kWh/L

(Note: the specific energy and energy density are the revised DOE 2010 hydrogen storage targets.)

Accomplishments

Identified soluble products of iridium catalyzed dehydrogenation of methylamine borane (MeAB) and ammonia borane (AB)/MeAB mixtures:

- Identified soluble products as mixtures of oligomers of varying chain lengths.
- Observed cross-linked products in the mixed AB/MeAB dehydrogenation reactions containing both (NH₂BH₂) and (CH₃NHBH₂) units.
- Collaborated with the Pacific Northwest National Laboratory (PNNL) to demonstrate an important capability for characterization of liquid spent fuel.
- Successfully extended the highly active (^tBuPOCOP) Ir motif to a first row metal (cobalt).
- Optimized the previously reported cobalt pre-catalyst and targeted more robust ligand motifs.
- Collaborated with the University of Oregon on CBN materials:
 - Transferred synthetic portion of effort to University of Oregon.
 - Began screening CBN materials provided by University of Oregon for dehydrogenation activity with known AB dehydrogenation catalyst.

Introduction

In order for chemical hydrogen storage to be feasible the storage materials must have a high weight percentage of hydrogen. Compounds containing carbon (C), boron (B) and nitrogen (N) are therefore promising. However, the discovery that dehydrogenation of B-N bonds is exothermic means that direct regeneration of spent BN fuel will not be possible. Dehydrogenation of C-C bonds is endothermic and this fact presents a potential opportunity for tuning the thermodynamics of dehydrogenation by mixing carbon, boron and nitrogen in the same material. We are working on developing and testing non-precious group metal (PGM) catalysts for rapid dehydrogenation of B-N and C-C bonds.

Approach

Our approach to meeting the DOE targets is to rationally design non-PGM catalysts for the dehydrogenation of amine borane systems. Through ligand modification we are able to tune the catalyst for increased stability and activity. We are also concerned with the viability of direct regeneration of amine borane materials which determines whether the material might be suitable for on-board regeneration. We have directly measured the enthalpy of dehydrogenation for a variety of amine borane systems and determined that it will not be possible to regenerate them directly by reaction with hydrogen. Collaborations have been initiated with the University of Oregon and University of Alabama to identify and synthesize novel CBN materials. Calculations (University of Alabama) have shown that several cyclic CBN materials have overall thermodynamics of dehydrogenation that are near thermoneutral. The Liu group at the University of Oregon are specialists in synthesizing heterocyclic CBN materials and we are working with them to develop catalysts that are capable of dehydrogenating both B-N and C-C bonds.

Results

Through a newly established collaboration with the Liu group at the University of Oregon we have received and started testing a new CBN heterocycle. Calculations from our collaborators at the University of Alabama suggest that dehydrogenation of CBN heterocycles such as 1,2-azaboracyclohexane will be endothermic and lead to overall thermodynamics near thermoneutral (see Figure 1). Preliminary dehydrogenation studies have been carried out on some of these materials. The first of these cyclic CBN compounds (CBN-1) has been shown to react with the previously successful dehydrogenation catalyst (^tBuPOCOP)IrH₂ (^tBuPOCOP

FIGURE 1. Dehydrogenation of 1,2-azaboracyclohexane and calculated enthalpy of reaction.

= [η^3 -1,3-(OP^tBu)₂C₆H₃]). Small amounts of the fully dehydrogenated product (CBN-2) were observed, however, only as a minor product. Additional dehydrogenation reactions will be attempted as the compounds are received from the University of Oregon.

Previously we have reported the dehydrogenation of AB, MeAB, and mixed AB/MeAB using the catalyst (^tBuPOCOP)IrH₂ [1]. The product of AB dehydrogenation was found to be consistent with the reported cyclic pentamer, [NH₂BH₂]₅ [2]. Further characterization of the soluble products of MeAB and mixed AB/MeAB dehydrogenation systems by electrospray-ionization mass spectrometry (ESI-MS) and gel permeation chromatography (in collaboration with PNNL) has now revealed that the soluble products of both MeAB and 1:1 AB/MeAB appear to be mixtures of oligomers [3]. In the case of MeAB dehydrogenation, the isotopic distribution patterns observed by ESI-MS are consistent with both cyclic oligomers of the form [CH₃NHBH₂]_n and linear oligomers of the form [CH₃NH₂BH₃][CH₃NHBH₂]_n[NH₂CH₃]. The majority of the oligomers appear to be in the 600-800 molecular weight (MW) range, although this distribution is likely concentration dependent. The ESI-MS of the 1:1 AB/MeAB dehydrogenation product shows a similar distribution of cyclic and linear oligomers, consistent with the formulas [NH₂BH₂]_x[MeNHBH₂]_y and [NH₂BH₂]_x[MeNHBH₂]_y[H₂], respectively. All of the observed distribution patterns can be described without x or y differing by more than 3, consistent with previous observation that AB and MeAB appear to react in an approximate 1:1 ratio.

We have also previously reported that dehydrogenation of 2:1 and 5:1 AB/MeAB mixtures results in both soluble and insoluble products. The ESI-MS characterization of the soluble products supports earlier observations that the reaction between AB and MeAB still approximates a 1:1 ratio in these reactions but shifts the distribution of oligomers, as identical isotopic distribution patterns are seen in the ESI-MS spectra but shift towards lower MW oligomers. The insoluble products of these reactions have also been characterized by infrared spectroscopy and are consistent with the previously reported pentamer.

Development of 1st row transition metal catalysts is imperative to reducing costs of H₂ storage. The successful Ir catalyst utilizes a phosphorus-carbon-phosphorus (P-C-P) type pincer ligand which has been

employed for the analogous Co complexes. Direct analogues to the active Ir species ($^{t\text{Bu}}\text{POCOP}\text{IrH}_2$ and $^{t\text{Bu}}\text{POCOP}\text{IrH}_4$) have been obtained using Co. These complexes are only stable at low temperatures. At room temperature and above, these complexes decompose to the thermally stable $^{t\text{Bu}}\text{POCOP}\text{Co}(\text{H})$ complex for which there is no Ir analogue. This form does not have adequate catalytic activity for AB dehydrogenation.

We have been studying the previously reported Co complex Co_1 in order to better understand and characterize the catalytically active species. Rapid dehydrogenation is observed with the addition of Co_1 to a tetrahydrofuran solution of AB. Under modest catalyst loadings (2.0 mol% Co) one equivalent of H_2 can be released in less than 4 minutes (see Figure 2). Notably however, there is an irreproducible induction period during which time Co_1 is converted to the highly active species. Studies to isolate and/or synthesize this highly active species have been unsuccessful, likely due to the instability of the species.

In order to circumvent the problem of catalyst instability we have targeted and synthesized more robust analogs of this successful system. In the interim a publication has appeared from a German research group with a similar P-N-P aliphatic pincer complex of ruthenium that is very active for AB dehydrogenation. The ligand of their study and the ligand we have prepared are closely related and so we expect to produce competent catalysts. We are currently synthesizing Fe and Co complexes with these more robust P-N-P ligands. This same ruthenium complex has also shown potential for dehydrogenation of B-H, N-H and C-H bonds.

Conclusions and Future Directions

Products from the dehydrogenation of AB, MeAB, and mixed AB/MeAB using the catalyst ($^{t\text{Bu}}\text{POCOP}$)

FIGURE 2. H_2 collection graph at 30°C for dehydrogenation of AB with 2 mol% Co_1. The idealized solvent free wt% of the system is depicted on the right hand axis.

IrH_2 have been positively identified. The fast Ir catalyst has provided us with mechanistic insight valuable to extending this reactivity to complexes with lower overall cost. We were successful in creating direct analogues of this system with Co; however, the accessibility of a thermally stable +2 oxidation state precludes its usefulness as a dehydrogenation catalyst. Other Co catalysts bearing pincer-type P-N-P ligands have been identified with impressive AB dehydrogenation activity. These catalysts have variable induction periods and poor catalyst lifetimes. We are currently working toward understanding and circumventing these shortcomings. We have also investigated dehydrogenation of novel CBN materials using ($^{t\text{Bu}}\text{POCOP}$) IrH_2 . These compounds are dehydrogenated substoichiometrically, making identification of new catalysts necessary for this application. We have identified promising leads for complexes of less expensive metals for catalytic dehydrogenation reactions and will test these materials in CBN dehydrogenation reactions.

FY 2009 Publications/Presentations

1. *Sigma Borane Complexes of Iridium: Synthesis and Structural Characterization.* Travis J. Hebden, Melanie C. Denney, Vincent Pons, Paula M. B. Picolli, Thomas F. Koetzle, Arthur J. Schultz, Werner Kaminsky, K.I. Goldberg, and D. M. Heinekey, *J. Am. Chem. Soc.* **2008**, 130, 10812.
2. *A Convenient One Pot Synthesis of di(t-butyl) phosphinic chloride.* Daniel F. Brayton, Karen I. Goldberg, Werner Kaminsky and D. Michael Heinekey. *Phosphorus, Sulfur, and Silicon and the Related Elements*, **2008**, 183(10), 2534.
3. *Iridium Catalyzed Dehydrogenation of Substituted Amine-Boranes: Kinetics, Thermodynamics and Implications for Hydrogen Storage.* Brandon L. Dietrich, Karen I. Goldberg, D. Michael Heinekey, Tom Autrey, John Linehan, *Inorganic Chemistry* **2008**, 47(19), 8583.
4. *Dihydrogen Complexes of Co Supported by Pincer Ligands.* Travis J. Hebden, Karen I. Goldberg, D. Michael Heinekey, Dmitri G. Gusev. Presented at the Inorganic Chemistry Gordon Conference, June 2009.
5. *Structural Investigations of Ir Pincer Complexes Relevant to Catalytic H_2 Release from the Chemical Hydrogen Storage Material H_3NBH_3 .* Travis J. Hebden, Karen I. Goldberg, D. Michael Heinekey, Karsten Krogh-Jespersen, Alan S. Goldman, Thomas J. Emge, John A. Cowan, Arthur J. Schultz. Presented at the 238th ACS National Meeting, Washington, D.C., August 2009.
6. *Dehydrogenation Catalysts for BN and CBN Hydrogen Storage Materials.* D. Michael Heinekey, Travis J. Hebden, Steven L. Matthews, Karen I. Goldberg, Brandon L. Dietrich, Anthony J. St. John. Presented at the 238th ACS National Meeting, Washington, D.C., August 2009.

7. Solutions for Chemical Hydrogen Storage:
Hydrogenation/Dehydrogenation of B-N Bonds.
Anthony J. St. John, Brandon L. Dietrich,
Travis J. Hebden, Steven L. Matthews, Karen I. Goldberg,
D. Michael Heinekey. Presented at the DOE Hydrogen
Program Annual Review Washington D.C., June 2008.

References

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2. Bøddeker, K.W.; Shore, S.G.; Bunting, R.K. *J. Am. Chem. Soc.* **1966**, *88*, 4396.
3. Dietrich, B.L.; Goldberg, K.I.; Heinekey, D.M.; Autrey, T.; Linehan, J.C. *Inorg. Chem.* **2008**, *47*, 8583.

IV.B.1j Chemical Hydrogen Storage using Ultra-High Surface Area Main Group Materials and the Development of Efficient Amine-Borane Regeneration Cycles

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Technical Barriers

This project addresses the following technical barriers from the Storage section (3.3) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) System Weight and Volume
- (B) System Cost
- (C) Efficiency
- (R) Regeneration Processes

Technical Targets

This project is conducting studies of light element nanoparticles and molecular compounds. Insights gained from these studies will be applied toward the design and synthesis of hydrogen storage materials that meet the following DOE 2010 hydrogen storage targets:

- Cost: \$4/kWh net
- Specific energy: 2 kWh/kg
- Energy density: 1.5 kWh/L

Objectives

Regeneration

- Provide new materials, compounds and support for chemical regeneration of amine-boranes (AB) or boron amides from B-X (X= halide or oxide) compounds.
- To develop a method of regenerating AB or other chemical hydrides from spent fuel with use of a metal formate/hydride cyclable system.
- To develop light element hydride nanomaterials:
 - Test light element hydride nanomaterials ability to transfer hydrogen using different spent fuel forms.
 - Test light element hydride nanomaterials for spent chemical hydride regeneration such as “AB” regeneration.

Release

- Enhancement of hydrogen release for chemical hydrides such as AB with light element hydride nanoparticles.
 - Produce light element hydride nanoparticles in a low-cost, high-yield method.

Accomplishments

Regeneration

- Further refined our generic route to tin monoformate synthesis; tin monoformates were identified as the most promising compounds for the metal formate/hydride cycle for regeneration.
- Synthesis and characterization of monomeric and one-dimensional tin formates to test the metal formate/hydride cycle; thermolysis reactions yielded non-CO₂ elimination or ambiguous reaction products.
- Tri-n-butyltin formate repeatedly yields tri-n-butyltin hydride under thermolysis conditions and can be easily prepared.
- NaSi and NH₄Br for regeneration of AB from spent fuel: Quantification of the production of AB by simple one pot method.
- Si-H nanoparticles for regeneration of AB from spent fuel: Quantification of the production of AB by application of nanoparticles.

Release

- Light element hydride nanomaterials to affect hydrogen release kinetics: nano-boron-nitrogen (BN) produced from mechanically activated hexagonal-BN mixed with AB show elimination of foam problem associated with release, lowering of the release temperature and a smaller enthalpy for the first release of H₂ from AB. Confirmed and quantified release and provided a hypothesis for the mechanism.
- Preliminary results on the synthesis of mesoporous BN.

Introduction

UC Davis has two efforts in support of the Chemical Hydrogen Storage Center of Excellence: nanomaterials and molecule development for regeneration of molecular-based chemical hydrogen materials and enhancement of hydrogen release. In order to help support the Center, the UC Davis group is providing two approaches to the regeneration cycle, working closely with Los Alamos National Laboratory (LANL) and the Pacific Northwest National Laboratory (PNNL) on strategies. For regeneration the UC Davis group investigated main group formate small molecules or hydride nanomaterials as low-cost reagents to convert B–O or B–X in one step to B–H, as is proposed for the metal formate/hydride cycle as part of the overall LANL regeneration scheme. The formate work which demonstrated a completed cycle to regenerate B–H bonds was carried out at UC Davis by Bobby Ellis. A paper describing this work in collaboration with that of John Gordon at LANL will be submitted shortly. A postdoc from UC Davis has been working at PNNL for the past year to enable more effective collaboration on the use of nanomaterials for regeneration. We have quantified the amount of AB that is regenerated by the reaction of hydrogen terminated Si nanoparticles versus NaSi + NH₄Br in a one pot reaction. We have also studied the affect of nanoscale hexagonal BN (nano-BN) as an additive for AB and have shown that it decreases the onset temperature for hydrogen release. Both the nano-BN and the AB:nano-BN samples were prepared by ball milling. The materials were characterized by X-ray powder diffraction, ¹¹B nuclear magnetic resonance (NMR), thermal gravimetric analysis/differential scanning calorimetry/mass spectrometry (TGA/DSC/MS), and the hydrogen release was measured by a volumetric gas burette system. Several beneficial effects of the mixtures of AB:nano-BN in comparison with neat AB were noted: these were the decrease of the dehydrogenation temperature, the decrease in NH₃ formation as well as the decrease of the exothermicity of hydrogen release with increasing the

nano-BN concentration. Mesoporous BN was prepared and characterized by scanning electron microscope (SEM) and Brunauer-Emmett-Teller.

Approach

Regeneration

Main Group Formate Compounds

- Synthesize main group formates. Investigate their interconversion with metal hydrides under mild reaction conditions with the object of creating a simple chemical cycle to regenerate B–H bonds in AB.

Light Element Hydride Nanomaterials

- Synthesize light element hydride nanomaterials such as hydrogen capped Si_{1-x}P_x and compared properties to hydrogen capped Si nanoparticles.

Release

- Enhancement of release kinetics with additional of BN nanomaterial (elimination of foaming problem related to hydrogen release of AB and reduction of ammonia release).
- Initiated the synthesis of mesoporous BN in order to optimize hydrogen release capabilities of AB.

Results

Regeneration

Main Group Formate Compounds

UC Davis is collaborating with LANL on the regeneration of B–X to B–H. The proposed cycle starts with a metal formate with the ejection of CO₂ to give the metal hydride. This is part of the overall regeneration scheme for AB, proposed by LANL. The goal of this research is to find a molecular compound that can be used in this cycle and then optimize the process. The tin monoformates with bulky substituents that we examined did not eliminate CO₂ under our thermolysis conditions. There was no indication of any gas evolution in the systems that formed 1-dimensional polymers in the solid state {C₆H₁₁ (Cy), CH₂C₆H₅ (Bn)} at elevated temperatures up to 200°C. The substituents with increased steric bulk that allowed for the isolation of monomeric tin formates {C₆H₂-2,4,6-Me₃ (Mes), C₆H₃-2,4,6-Me₂ (Dmp)} resulted in CO ejection to yield tin hydroxides when heated at elevated temperatures. We have had success, however, with the less bulky tri-n-butyltin formate {Bu₃SnOC(O)H}, which results in the formation of a tin hydride under

thermolysis conditions. $\text{Bu}_3\text{SnOC(O)H}$ is readily prepared by treatment of Bu_3SnCl with equimolar amounts of HOC(O)H and NEt_3 . The reaction proceeds rapidly with the precipitation of $(\text{HNEt}_3)\text{Cl}$ that is easily removed. This procedure eliminates the need to isolate the tin oxide, which would be used to generate the tin formates by treatment with formic acid. Distillation of the resulting tin formate under vacuum through a column packed with glass beads yields the tin hydride Bu_3SnH . We are currently optimizing the reaction conditions to maximize the yield of the tin hydride.

Light Element Hydride Nanomaterials

We have explored the regeneration of B–H bonds from a B–O model system, by reacting nanoparticles of hydrogen terminated Si and $\text{NaSi} + \text{NH}_4\text{Br}$ with B(OPh)_3 in solution. The most promising reaction is provided:

This reaction provided new resonances in the ^{11}B solution NMR consistent with the products indicated above, along with a small amount of AB. However, we were not able to optimize the reaction products further and have abandoned this approach.

We have also been exploring the regeneration of spent fuel with both hydrogen terminated Si nanoparticles and directly from NaSi and NH_4Br . ^{11}B decoupled NMR indicates that AB can be generated at 60°C in 5 hours according to the reaction:

Release

We fully characterized nano-BN prepared by mechanical alloying and quantified the hydrogen release of AB when nano-BN was used as an additive. The initial work demonstrating the reduction in hydrogen release temperature, reduction in enthalpy of hydrogen release has been published. We have also designed a low-cost approach to the synthesis of mesoporous BN as a possible “scaffold” for AB. SEM results suggest that the synthesis is successful.

Conclusions and Future Directions

This project is relevant to the Center’s goals of recycling spent chemical hydride and AB regeneration. The approach provides novel nanomaterials and the synthesis of metal hydrides for efficient AB regeneration. We have made progress on two major areas that are part of the overall Center goals, collaborating with LANL and PNNL.

Regeneration: Demonstrated conversion of boron halide to boron hydride using a recyclable tin formate/tin hydride system. Demonstrated regeneration of AB from spent fuel via reaction with $\text{NaSi} + \text{NH}_4\text{Br}$ in simple one pot method.

Release: Light element hydride nanomaterials to affect hydrogen kinetics: preliminary results show elimination of foam problem associated with release, lowering of the release temperature, smaller enthalpy for the first release of H_2 from AB. The ratio of nano-BN:AB has been optimized. Delay in hydrogen release at temperature is eliminated. Preliminary understanding of the effect of nano-BN accomplished through high field NMR, high resolution transmission electron microscopy, TGA/DSC/MS, Fourier transform infrared, and Raman spectroscopy. Prepared mesoporous BN and verified via SEM characterization.

In terms of technology transfer/collaborations, we have active partnerships with LANL, PNNL, and University of Alabama and have provided the results to the wider scientific public by means of presentations, publications, and patent applications. We initiated collaboration with SigNa, a start-up company that has developed an inexpensive route to NaSi , which we have explored as a useful hydrogen generation agent during this time period.

Future directions include understanding the reaction of $\text{NaSi} + \text{NH}_4\text{Br}$ for possible regeneration ability and the effect of catalysts and mesoporous BN on hydrogen release of AB.

Regeneration

- Main group formate compounds.
 - Develop a method of M-H recycling via hydrogenolysis as an alternative to the metal formate/hydride approach.
- Light element hydride nanomaterials.
 - Gain a better understanding through NMR and other spectroscopies as to why spent fuel can be almost fully regenerated, but B(OR)_3 cannot.
 - Quantify the reaction of spent fuel for production of AB. Optimize reaction parameters.

Release

- Further optimization of light element nanoparticles (such as BN) to reduce foam and to affect the hydrogen release kinetics without adding contamination, additional weight, and regeneration issues.
- Addition of catalyst for AB release to the nano-BN.
- Preparation of meso-BN in order to further optimize the effect of nano-BN upon hydrogen release from AB. This will take advantage of higher surface area.

FY 2009 Publications/Presentations

1. *Promotion of Hydrogen Release from Ammonia Borane with Mechanically Activated Hexagonal Boron Nitride*, D. Neiner, A. Karkamkar, J.C. Linehan, B. Arey, T. Autrey, and S.M. Kauzlarich, *J. Phys. Chem. C*, **2009**, *113*, 1098-1103.
2. *Nanomaterials as Additives for Hydrogen Release from Ammonia Borane*, S. M. Kauzlarich, oral presentation at the NEDO Hydrogen Storage Meeting, 8–10 September 2008.
3. *Promotion of hydrogen release from ammonia borane with nanostructured hexagonal boron nitride* S.M. Kauzlarich, invited oral presentation at the 237th ACS National Meeting, Division of Industrial & Engineering Chemistry, Nanotechnology and the Environment: Emphasis on Green Nanotechnology, Salt Lake City, UT, March 22-26, 2009, Paper number: 128.

IV.B.1k Electrochemical Hydrogen Storage Systems

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Contract Number: DE-FC36-05GO15054

Subcontractor:
George Engelhardt, OLI Systems, Morris Plains, NJ.

Project Start Date: March 1, 2005
Project End Date: September 30, 2009

Objectives

- Demonstrate and characterize electrochemical transformations of ammonia borane (AB) and organotin hydrides.
- Investigate direct hydrogenation of AB in ionic liquids.
- Further develop electrochemical impedance spectroscopy (EIS) as a tool for mechanistic analysis of electrochemical systems.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) System Weight and Volume
- (C) Efficiency
- (R) Regeneration Processes

Technical Targets

Electrochemistry of AB and Organotin Hydrides

Our task is to determine the electrochemical behavior of AB and discover whether an electrochemical route to regenerating the spent AB fuel is possible. The regeneration of spent AB fuel is being investigated directly (without outside reducing agents) and indirectly (with organotin hydrides as an intermediate reducing agent). If the indirect route is chosen, we need to be able to regenerate the oxidized form of the organotin hydride in order to make the project a success.

Direct Hydrogenation of AB in Ionic Liquids

In addition to aqueous and organic solutions, we are attempting the direct hydrogenation of spent AB fuel (or organotin halide) in ionic liquids. Because we have no spent fuel at this time, a test hydrogenation process is being used to verify that the technique works. As such, we picked the hydrogenation of carbon dioxide (CO_2) to methanol in ionic liquid as our test system.

Mechanistic Analysis using EIS

In conjunction with other experiments, EIS can be used to identify the reaction mechanism of the system under study. By creating a general model and computer code for EIS, we can now extract kinetic parameters from reactions we are investigating. This will allow us in the future to optimize experimental conditions to achieve maximum reaction rates for systems of interest to this project.

Accomplishments

- Demonstrated complex electrochemical activity of AB.
- Attempted the hydrogenation of organotin halide using direct electrolysis techniques as well as beginning work to hydrogenate organotin halide in the Devanathan cell.
- Successfully hydrogenated several samples of styrene using the Devanathan cell in preparation for receiving samples of spent AB fuel.
- Finished the design and testing of a non-aqueous reference electrode to enable accurate potential measurements in organic solvents.
- Attempted direct hydrogenation of carbon dioxide in ionic liquids.
- Finished testing our general model of electrochemical impedance spectroscopy on a

simple reaction and successfully extracted kinetic information by a best-fit procedure.

Introduction

AB is a material capable of reaching DOE 2010 and 2015 goals for volumetric and gravimetric hydrogen storage densities. After the extraction of hydrogen from AB, the spent fuel needs to be regenerated in order for the overall process to continue. The spent AB fuel is polymeric in form and it can be digested using techniques from other researchers within the Chemical Hydrogen Storage Center of Excellence. The digested material can then be hydrogenated either directly using electrochemical regeneration or by reacting it with a reducing agent such as an organotin hydride [1]. If the latter method is used, the organotin hydrides become oxidized at the expense of hydrogenating the spent AB fuel, and as such the organotin compounds will need to be hydrogenated (electrochemically). Our work is being investigated in aqueous, organic (non-aqueous), and ionic liquid conditions.

Because many important reactions in this research are not fully understood, we want to be able to discover the exact reaction mechanism as well as the important kinetic parameters that control the overall system. Once the reaction mechanism and kinetic parameters are known for a system of interest, it would then be possible to setup the experimental conditions in such a way as to optimize the reaction rates, which would lead to increased efficiency.

Approach

Our focus for the hydrogenation of AB spent fuel will be to utilize a Devanathan cell for electrochemical reduction (hydrogenation) reactions. The Devanathan cell (shown in Figure 1) is a two- or three-compartment cell (depending on whether an additional solution separator is used) that uses a palladium or palladium alloy foil as the main solution separator as well as the working electrode for the hydrogenation reactions. The Devanathan cell works by generating hydrogen on one surface of the palladium foil and allowing it to diffuse through the foil (by chemical potential gradient) to the reaction side, where the hydrogen is supplied to hydrogenate the solution species either chemically or electrochemically. Because the Devanathan cell is not typically used to hydrogenate samples (its typical use is to study hydrogen diffusion through the membrane), we needed to test the process and chose the hydrogenation of styrene as an example until we receive spent AB fuel to study. We have also recently started using this technique to attempt the hydrogenation of organotin halides to support the indirect method of hydrogenation.

FIGURE 1. Schematic diagram of the Devanathan-Stachurski cell. In the styrene hydrogenation reactions, we do not need a separator membrane or a counter electrode on the reaction side since the hydrogenation occurs chemically. Also, for this work, we are using 6 M KOH as opposed to 1 M H_2SO_4 on the charging side.

In addition to the Devanathan cell work, we have also attempted the direct hydrogenation method in ionic liquid solutions. Again, because we do not have spent AB fuel to study, we have worked with the hydrogenation of carbon dioxide as a test reaction. To support both the direct and indirect hydrogenation methods, we have developed (in conjunction with Dr. George Engelhardt of OLI Systems) a general mathematical model of electrochemical impedance spectroscopy and a computer program to simulate and best-fit results based on the reaction mechanism. The mathematical modeling of reaction mechanisms will be applied to the AB and organotin hydride samples.

Results

In light of the findings from literature [2-7], our work has employed both acetonitrile (ACN) and dimethoxyethane (glyme) as solvents. We consider the electrochemical activity of hexaalkyldistannane to be important. This is because most radicals are highly reactive species and thus their reactions have very low activation energies. Furthermore, in contrast to ionic reactions, solvent effects are rather minimal in the vast majority of radical reactions. For these reasons, we speculate that little can be done to avoid dimerization of trialkyltin radicals and therefore conditions must be chosen to allow the reduction of hexaalkyldistannanes. Most of the work in the literature has used either mercury or amalgamated working electrodes; we used these in some experiments. Additionally, a silver working electrode was used in some experiments. Silver was chosen because it is known to be a good electrocatalyst for the reduction of alkyl halides, and therefore it would be interesting to see if it exhibits similar behavior in the reduction of trialkyltin halides [8].

Figure 2 shows cyclic voltammograms (CVs) obtained at a 1 mm silver disk working electrode

FIGURE 2. CV at 1 mm diameter silver disk working electrode. Sweep rate: 250 mV/s. CE: platinum wire. RE: Pt pseudo-reference. Blue: blank (0.1 M TBAPF₆ in glyme). Red: 10 mM Bu₃SnCl in 0.1 M TBAPF₆/glyme. Arrows indicate direction of sweep. The labels are described in the text.

for 10 mM tributyltin chloride (Bu₃SnCl) in 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆)/glyme. A large amount of electrochemical activity is evident in the CV of 10 mM Bu₃SnCl. Peak C1, a cathodic peak, occurs on the forward sweep near -3 V. Peak C2 is most likely related to peak A2. The identity of peak A2 is not clear. The shape and location suggests that it is related to the oxidation of solvent (glyme) or supporting electrolyte (TBAPF₆). On the other hand, this peak is not seen in the blank. However, since a platinum wire is being used as a pseudo-reference, the potential scale may have shifted upon addition of the Bu₃SnCl. Peak C3 is seen here as what appears to be two closely-spaced peaks. In some experiments, however, it appears as one broad peak. The reason for this behavior is not clear at this time. By analogy to the results of Mazzocchin's group, it would seem that this peak is due to reduction of Bu₃SnCl to Bu₃Sn radical. Peak C5 or C6 look similar to the peak observed by Mazzocchin et al. for Ph₃SnCl in ACN. These workers attributed the peak to reduction of Ph₃SnSnPh₃, which formed by dimerization of Ph₃Sn radicals (described above).

Some experiments were performed where phenol (PhOH) was added to the electrolyte solution. Some of these experiments employed holds for various times at potentials corresponding to various peaks (particularly C5 and C6), but no evidence of Bu₃SnH formation was found in the voltammograms. Exploratory CV was performed on a ~13 mM Bu₃SnSnBu₃ solution; the CVs are shown in Figure 3. In these CVs, no peak corresponding to Bu₃SnSnBu₃ reduction is seen. However, when comparing the red curve (Bu₃SnSnBu₃) with the green curve (Bu₃SnSnBu₃ with PhOH), a significant change is evident. The CV for Bu₃SnSnBu₃

FIGURE 3. CV at 1 mm diameter silver disk working electrode. Sweep rate: 300 mV/s. CE: platinum wire. RE: Pt pseudo-reference. Blue: blank (0.1 M TBAPF₆ in glyme). Red: ~13 mM Bu₃SnSnBu₃ in 0.1 M TBAPF₆/glyme. Green: ~13 mM Bu₃SnSnBu₃ with 10 mM PhOH in 0.1 M TBAPF₆/glyme.

shows three anodic peaks on the forward sweep. After addition of PhOH, these peaks are extinguished.

The meaning of the results of these CV experiments is not clear at this time. As mentioned above, peak C5 or C6 in Figure 2 resemble the peak attributed to Ph₃SnSnPh₃ reduction observed by Mazzocchin et al. However, when a known sample of Ph₃SnSnPh₃ was used, this peak was not evident. Perhaps C5 or C6 are not due to reduction of Bu₃SnSnBu₃. Evidently, more experiments to identify the source of these peaks are required.

To test the Devanathan cell, we attempted the hydrogenation of styrene, which is known to form ethylbenzene. The reaction was carried out by applying a fixed current to the palladium alloy membrane for various periods of time. An analysis using gas chromatography-mass spectrometry revealed that the rate of production (hydrogenation) is 2.90% per day at an average efficiency of 79%, see Figure 4.

The technique used to monitor the hydrogenation of CO₂ in ionic liquids was CV; and this was carried out with a computerized electrochemical workstation (Gamry Instrument). To analyze the reaction product, Fourier transform infrared-attenuated total reflectance spectroscopy has been employed.

All experiments were carried out in 0.01 M 1-butyl 3-methyl imidazolium hexafluorophosphate aqueous solution. A platinum metal plate was employed as a working electrode. The surface of the electrode was etched by hot concentrated sulfuric acid. The electrode potential of the cathode was measured with respect to Ag/AgCl (sat. KCl) reference electrode. A platinum wire was used as counter electrode. Pure N₂ gas

FIGURE 4. Gas chromatography–mass spectroscopy results for a sample of styrene that was hydrogenated using the Devanathan cell.

was bubbled into the solution for an hour to remove dissolved oxygen. The electrolysis was carried out in a closed U-cell and the solvent was saturated with CO_2 for 120 minutes. The cell was usually operated at room temperature under H_2 atmosphere. The cyclic voltammetry responses for platinum plate in CO_2 saturated ionic liquid solution are featureless over the potential region between 0.5 to -0.3 V.

We have tested our general model of EIS using real data collected from the reduction of ferricyanide anion to ferrocyanide anion as a known reaction. Our results are in excellent agreement with those found in literature and we are continuing to improve our model to include better fitting algorithms.

Conclusions and Future Directions

- The electrochemical behavior of organotin halide/hydride systems is not fully understood, however it appears to be possible to successfully hydrogenate organotin halides to their respective hydride using electrolysis or Devanathan cell techniques.
- The direct hydrogenation of carbon dioxide (as a test system) was attempted in ionic liquids, however the results did not indicate any hydrogenated species.

- Our general mathematical model of EIA has been tested on real data and yields very good results.
- Future work includes Devanathan cell reduction reactions of organotin halides, improved techniques for ionic liquid direct hydrogenation, and more complex testing of the EIS model using another known reaction from the literature.

FY 2009 Publications/Presentations

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2. S. Colominas, J.B. McLafferty, and D.D. Macdonald, "Electrochemical Studies of Sodium Borohydride in Alkaline Aqueous Solutions Using a Gold Electrode," *Electrochim. Acta*, in press (2009).
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4. J.C. Tokash, G.R. Engelhardt, and D.D. Macdonald, "On the Development of a General Electrochemical Impedance Model," *Transactions of the Electrochemical Society*, in preparation (2009).

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IV.B.1I Chemical Hydrogen Storage Using Polyhedral Borane Anions and Aluminum-Ammonia-Borane Complexes

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Contract Number: DE-FC36-05GO15058

Project Start Date: September 2005
Project End Date: March 2010

- (A) System Weight and Volume
- (B) System Cost
- (C) Efficiency

Technical Targets

Phase II - Al-AB Complexes:

- This project is directed towards evaluating Al-AB complexes as candidates for hydrogen storage. The hydrogen release studies on these complexes coupled with Center's efforts on other AB materials will be targeted towards the design and synthesis of hydrogen storage materials that meet the following DOE 2010 hydrogen storage targets:
 - Cost: \$/kWh net
 - Specific energy: 1.5 kWh/kg
 - Energy density: 0.9 kWh/L
- (Note: the specific energy and energy density are the revised DOE 2010 hydrogen storage targets.)

Objectives

Phase I

- Develop heterogeneous catalysts for the controlled generation of hydrogen from the hydrolysis of salts of $B_{12}H_{12}^{2-}$, $B_{10}H_{10}^{2-}$ and $B_{11}H_{14}^{-}$ ions.
- Determine the kinetics and mechanism of these catalyzed borane anion hydrolysis reactions to provide design data for large-scale hydrogen generation devices.

Phase II

- Synthesize and evaluate aluminum-ammonia-borane (Al-AB) complexes as hydrogen storage candidates.
- Carry out hydrogen release studies on Al-AB complexes by thermal dehydrogenation process.
- Investigate the regeneration of the spent material.

Technical Barriers

This project addresses the following technical barriers from the Storage section (3.3.4) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

Accomplishments

- Synthesized various Al-AB complexes. These include $Al(NH_2BH_3)_3$, $LiAl(NH_2BH_3)_4$ and their ammonia adducts.
- Conducted initial hydrogen release experiments on these complexes by thermal dehydrogenation process. $Al(NH_2BH_3)_3$ complex starts releasing hydrogen at 60°C. The $LiAl(NH_2BH_3)_4$ complex and ammonia adduct of $Al(NH_2BH_3)_3$ generate hydrogen at 100°C.
- Discovered that ammonia adduct of $Al(NH_2BH_3)_3$ also releases NH_3 when heated above 80°C.
- Preliminary differential scanning calorimetric (DSC) studies on $Al(NH_2BH_3)_3$ indicate that the hydrogen release from this complex is exothermic and will require off-board regeneration.

Introduction

The phase I of the University of Missouri efforts were directed towards investigating catalytic hydrolysis of polyhedral borane anions for hydrogen generation. This project was down-selected in year 2008. The phase II of the project is directed towards evaluating Al-AB complexes as chemical hydrogen candidates.

The AB molecule is a demonstrated source of chemically stored hydrogen, which can meet DOE performance parameters except for its regeneration from spent AB and elemental hydrogen. Our project is focused on the synthesis and evaluation of AB derivatives containing aluminum as a structural component since some direct reactions of aluminum and its derivatives with dihydrogen are known processes which yield Al-H intermediates and products. Consequently, the presence of an aluminum center bonded to multiple AB residues might combine the efficiency of AB dehydrogenation with an aluminum mediated hydrogenation process leading to reversibility. Other modifications could also be used to test for reversible regeneration such as the introduction of transition metal catalysts and the use of ionic liquid solvation. Figure 1 illustrates hydrogen capacity of AB and metal ammonia-borane (M-AB) complexes.

Approach

In the phase II of the project the center has focused its efforts on developing amino boranes and M-AB complexes as candidates for chemical hydrogen storage. The project at the University of Missouri is focused upon developing Al-ABs as sources for hydrogen fuel generation, specifically their synthesis, dehydrogenation and regeneration studies. Initially we have concentrated our efforts on the synthesis of $\text{Al}(\text{NH}_2\text{BH}_3)_3$, $\text{LiAl}(\text{NH}_2\text{BH}_3)_4$ and their ammonia adducts. Figure 1 shows the theoretical hydrogen wt% capacity for AB and various metal amido boranes. The Al-AB complexes have comparable hydrogen capacity with other M-ABs and have potential to meet DOE's 2010 and 2015 targets for system wt%.

Results

During the last year we investigated a number of routes to synthesize Al-AB complexes. Of these routes, the reaction of $\text{M}(\text{NH}_2\text{BH}_3)_n$ where $\text{M} = \text{Li}, \text{Na}$ or K with AlCl_3 gave the desired $\text{Al}(\text{NH}_2\text{BH}_3)_3$ complex. The $\text{M}(\text{NH}_2\text{BH}_3)_n$ were prepared from the reaction of NH_3BH_3 with corresponding metal hydrides. The reaction of $\text{Li}(\text{NH}_2\text{BH}_3)_3$ with AlCl_3 at low temperature gives $\text{Al}(\text{NH}_2\text{BH}_3)_3$ in good yield, but the isolation of the pure product is complicated. Alternatively, the reaction

FIGURE 1. Hydrogen Capacity for AB and M-AB

of $\text{Na}(\text{NH}_2\text{BH}_3)_3$ with AlCl_3 proceeded well to give Al-AB in 70% yield. The purity of the material was confirmed by ^{11}B and ^{27}Al nuclear magnetic resonance (NMR) and infrared (IR) spectroscopy.

General Procedure for the Synthesis of $\text{Al}(\text{NH}_2\text{BH}_3)_3$

The reaction was carried out by adding a solution of AlCl_3 in glyme to a solution of M-AB ($\text{M} = \text{Li}, \text{Na}$ or K) at -10°C over a period of 30 minutes. The reaction was further stirred for 4 h at -10°C . The reaction was monitored by observing the ^{11}B NMR spectrum of a sample of the reaction mixture. Completion of the reaction is indicated by the disappearance of M-AB peak at 20.2 ppm. The reaction mixture was filtered and the solvent was removed under vacuum. The resulting solid was washed with a mixture of glyme and diethyl ether to give $\text{Al}(\text{NH}_2\text{BH}_3)_3$ in approximately 70% yield. The product $\text{Al}(\text{NH}_2\text{BH}_3)_3$ was characterized by ^{11}B , ^1H and ^{27}Al NMR and IR spectroscopy (Figure 2).

Synthesis of $\text{NH}_3 \cdot \text{Al}(\text{NH}_2\text{BH}_3)_3$ Adduct

The ammonia adduct of $\text{Al}(\text{NH}_2\text{BH}_3)_3$ was synthesized by reacting $\text{Al}(\text{NH}_2\text{BH}_3)_3$ with excess of ammonia in tetrahydrofuran and isolated as an insoluble precipitate.

The complex was characterized by solid-state ^{11}B NMR and IR spectroscopy. A powder X-ray diffraction study showed that the ammonia adduct is structurally similar to the parent $\text{Al}(\text{NH}_2\text{BH}_3)_3$ complex and suggests that the ammonia is incorporated in the unit cell by hydrogen bonding. To gain more insight into the structure of this ammonia adduct we are synthesizing various amine complexes of $\text{Al}(\text{NH}_2\text{BH}_3)_3$ which will be soluble in common organic solvents and will be more

FIGURE 2. ^{11}B NMR Characterizations of Al-AB Complexes

suitable for structural characterization studies including single crystal X-ray diffraction analysis.

Synthesis of $\text{LiAl}(\text{NH}_2\text{BH}_3)_4$

The synthesis of $\text{LiAl}(\text{NH}_2\text{BH}_3)_4$ was achieved by reacting LiAlH_4 with AB at room temperature for 24 h. The product was characterized by ^{11}B and ^{27}Al NMR spectra and IR spectroscopy.

The reaction of this $\text{LiAl}(\text{NH}_2\text{BH}_3)_4$ with liquid ammonia gave a white precipitate. Further structural characterization of this precipitate is currently underway.

Thermal Dehydrogenation Studies on Al-AB Complexes

Figure 3 shows the thermogravimetric analysis-mass spectrometer (TGA-MS) analysis of Al-AB complexes.

These studies done at Los Alamos National Laboratory show that $\text{Al}(\text{NH}_2\text{BH}_3)_3$ releases hydrogen at 60°C and the ammonia adduct $\text{NH}_3 \cdot \text{Al}(\text{NH}_2\text{BH}_3)_3$ generates hydrogen at 100°C. The ammonia adduct also releases ammonia at 100°C. The $\text{LiAl}(\text{NH}_2\text{BH}_3)_4$ complex starts releasing hydrogen at 110°C and peaks at around 170°C. A DSC analysis on $\text{Al}(\text{NH}_2\text{BH}_3)_3$ indicates that the hydrogen release process is exothermic and therefore will require an off-board regeneration process.

Hydrogen release experiments on $\text{Al}(\text{NH}_2\text{BH}_3)_3$ and $\text{LiAl}(\text{NH}_2\text{BH}_3)_4$ complexes were carried out by heating the complexes to 190°C in the absence of solvent or a catalyst. A plot of moles of hydrogen released vs. temperature is shown in Figure 4. In the case of $\text{Al}(\text{NH}_2\text{BH}_3)_3$ complex, approximately 4.1 moles of hydrogen is released at 190°C, which corresponds to about 6 wt% hydrogen based on material wt%. The $\text{LiAl}(\text{NH}_2\text{BH}_3)_4$ complex under similar experimental conditions released approximately 5.2 moles of hydrogen

FIGURE 3. TGA-MS, DSC and Powder X-ray Study of Al-AB Complexes

FIGURE 4. Thermal Dehydrogenation of $\text{Al}(\text{NH}_2\text{BH}_3)_3$ and $\text{LiAl}(\text{NH}_2\text{BH}_3)_4$ Complexes

which corresponds to around 7 wt% hydrogen based on material wt%. Further detailed quantitative hydrogen release measurements in the presence of a catalyst as well as kinetic studies on these Al-AB complexes are currently being carried out in our laboratories.

Conclusions and Future Directions

Al-AB complexes are viable candidates for chemical hydrogen storage. Our preliminary studies show that they can be easily synthesized from AB precursors and they are capable of generating hydrogen at lower temperature than AB alone.

- Synthesis of Al-AB complexes was achieved.
- Dehydrogenation in the absence of a catalyst show that they can generate hydrogen up to 7 wt%.

- TGA-MS analysis on the ammonia adduct of $\text{Al}(\text{NH}_2\text{BH}_3)_3$ showed that ammonia is also released when the complex is heated above 100°C.

Future Studies

- Carry out detailed hydrogen release experiments and conduct kinetic studies on the dehydrogenation process.
- Improve the hydrogen generation rate at lower temperature.
- Identify a suitable catalyst for dehydrogenation process.
- Identify spent material and investigate metal hydride mediated regeneration of the spent material.
- Structurally characterize Al-AB complexes.

FY 2009 Publications/Presentations

1. Poster presentation at DOE annual merit review, Washington, D.C., May 2009.

IV.C.1a Overview of the DOE Hydrogen Sorption Center of Excellence

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- California Institute of Technology (Caltech), Channing Ahn
- Duke University, Jie Liu
- Lawrence Livermore National Laboratory (LLNL), Ted Baumann and Joe Satcher
- National Institute of Standards and Technology (NIST), Dan Neumann and Craig Brown
- Oak Ridge National Laboratory (ORNL), Dave Geohegan
- Pennsylvania State University (PSU), Peter C. Eklund, Michael Chung, Henry Foley, and Vin Crespi
- Rice University, James Tour, Carter Kittrell, and Richard E. Smalley (deceased)
- Rice University, Boris Yakobson and Robert Hauge
- Texas A&M University (TAMU) Hongcai Zhou (formerly of Miami University-Ohio)
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Project Start Date: February 1, 2005
Project End Date: Project continuation and direction determined annually by DOE

in the tank with minimum energy requirements and minimum penalties to the hydrogen fuel infrastructure. Work is directed at overcoming barriers to DOE system goals and identifying pathways to meet the hydrogen storage system targets. In particular, the HSCoE strives to:

- Develop high-specific-surface-area sorbent materials with optimal H binding energies with the focus to increase binding up to ~25 kJ/mol H₂ for room temperature operation. This enables:
 - High-capacity systems that operate at modest pressures (e.g., less than 100 bar) and below fuel-cell operating temperatures (<70°C).
 - Meeting both gravimetric and volumetric targets simultaneously with rapid kinetics.
 - Efficient and rapid on-board refueling with minimum energy requirements.
- Rapidly correlate capacity, structural, and energetic information to reduce time between discovery, assessment, and down-selection of materials.
 - Integrate experiment and theory seamlessly in both “feedback” (explanation) and “feed-forward” (discovery) modes.
 - Devise facile synthetic routes using low-cost approaches.
- Create a nimble and flexible, yet structured, teaming environment to accelerate discovery, evaluation, and selection of promising development directions.
 - Partners are organized in focused groups to optimize development and avoid duplication of effort, with seamless integration of experiment/theory.
 - Quantitative down-select criteria are used prior to beginning research and development and at Go/No-Go points.

Technical Barriers

The HSCoE is developing novel high-surface-area hydrogen storage materials for advanced fuel cell technologies. The HSCoE presently has 15 active projects at 18 institutions. HSCoE partners are conducting a wide range of applied research and engineering studies on currently available sorbent materials and developing design principles and synthetic methods for next-generation materials that will meet the critical DOE system hydrogen storage targets. The technical barriers addressed by these projects from the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan include:

Objectives

The Hydrogen Sorption Center of Excellence (HSCoE) seeks to discover and develop high-capacity sorbent materials that can operate at ambient temperatures and be efficiently and quickly charged

General:

- (A) System Weight and Volume
- (B) System Cost
- (C) Efficiency
- (D) Durability/Operability
- (E) Charging/Discharging Rates
- (J) Thermal Management

Reversible On-Board:

- (P) Lack of Understanding of Hydrogen Physisorption and Chemisorption
- (Q) Reproducibility of Performance

Technical Targets

The HSCoE is developing sorption materials for hydrogen storage systems. As shown in Table 1, the HSCoE is focused on addressing the higher-risk targets for sorbents that are associated with capacity and costs, including:

- Cost: \$4/kWh net
- Specific energy: 1.8 kWh/kg
- Energy density: 1.3 kWh/L
- Charging/Discharging Rate: 3.3 min

Accomplishments

The HSCoE partners work closely together to systematically accelerate the development of advanced hydrogen sorbent materials. For specific details, please review their individual contributions to this report. A summary of representative accomplishments is listed as follows.

- The HSCoE partners work in close coordination performing focused development of hydrogen storage materials. The coordination activities included:
 - Materials-development selection criteria were created for different materials classes to provide guidance regarding whether a given development effort should proceed.

TABLE 1. Status of Sorption Materials' Ability to Meet DOE System Storage Targets

Storage Parameter	Units	2010	2015	Ultimate
System Net Gravimetric	kWh/kg (kg H ₂ /kg system)	1.5 (0.045)	1.8 ^M (0.055)	2.5 ^H (0.075)
System Volumetric Capacity: Usable energy density from H ₂ (net useful energy/max system volume)	kWh/L (kg H ₂ /L system)	0.9 (0.028)	1.3 ^M (0.040)	2.3 ^H (0.070)
Storage System Cost (and fuel cost)	\$/kWh net (\$/kg H ₂) \$/gge at pump	4* (133) 2-3	2* ^M (67) 2-3 ^M	TBD ^H 2-3 ^H
Durability/Operability <ul style="list-style-type: none"> Operating ambient temperature Min/max delivery temperature Cycle life (1/4 tank to full) Cycle life variation Min delivery pressure from storage system; FC= fuel cell, ICE= internal combustion engine Max delivery pressure from storage system 	°C °C Cycles % of mean (min) at % confidence atm (abs) atm (abs)	-30/50 (sun) -40/85 1,000 90/90 4FC/35 ICE 100	-40/60 (sun) -40/85 1,500 99/90 3FC/35 ICE 100	-40/60 (sun) -40/85 1,500 99/90 3FC/35 ICE 100
Charging/Discharging Rates <ul style="list-style-type: none"> System fill time (for 5-kg H₂) Minimum full flow rate Start time to full flow (20°C) Start time to full flow (-20°C) Transient response 10%-90% and 90% -0% 	min (kg H ₂ /min) (g/s)/kW s s s	4.2 min (1.2 kg/min) 0.02 5 15 0.75	3.3 min (1.5 kg/min) 0.02 5 15 0.75	2.5 min (2.0 kg/min) 0.02 5 15 0.75
Fuel Purity (H ₂ from storage)	% H ₂	99.99 (dry basis)		
Environmental Health & Safety <ul style="list-style-type: none"> Permeation & leakage Toxicity Safety Loss of useable H₂ 	scc/h - - (g/h)/kg H ₂ stored	Meets or exceeds applicable standards		
		0.1	0.05 ^M	0.05 ^M

*The storage system costs are currently under review and will be changed at a future date.

Unmarked: low risk, high probability to meet; M: medium risk, medium probability to meet; H: high risk, low probability to meet.

TBD - to be determined.

- Technology development “roadmaps” were updated to reflect progress toward addressing DOE’s Multi-Year Research, Development, and Deployment Plan.
- The HSCoE is completing a materials Go/No-Go recommendation document that will feed into the final report for the center.
- The HSCoE developed and applied advanced and new spectroscopic techniques to determine the relationships between material structure and hydrogen storage behavior.
- NIST determined bulk elemental compositions of materials of interest to the HSCoE using prompt gamma analysis, and employed inelastic neutron-scattering methods to determine the location of hydrogen-binding sites and the site-specific hydrogen adsorption strength in several different materials. Materials studied included metal-decorated, carbon-based materials; metal organic frameworks (MOFs); and boron-infused carbon materials. This understanding helps to speed sample development and material synthesis aimed at reaching the DOE targets.
- NIST illustrated the site-specific hydrogen adsorption strength in MOF materials. The overall appreciation of this determines the isosteric heats of hydrogen adsorption. The size and shape of the Coulomb potential determines inelastic neutron-scattering features. Spectra are composed of rotations and multiple rotation-phonon transitions.
- UNC performed ^1H nuclear magnetic resonance (NMR) and ^{11}B NMR spectroscopy to evaluate the porosimetry of materials using H_2 as the probe molecule, and also to evaluate boron site symmetry in various boron-substituted materials. UNC demonstrated unexpectedly large crystal fields promoting strong binding and/or trapping to produce high H_2 capacity in MOFs. UNC determined that the nature of activated polyether ether ether ketone (PEEK)-adsorbing surfaces remains unchanged even for material with the highest burn-off value. UNC also determined that opened single-walled nanohorn (SWNH) materials confine H_2 in an interconnected space composed of interstitial and endohedral sites. Adsorption occurs predominantly in the interstitial volume at low pressure with the endohedral volume being filled with increasing pressure.
- NREL improved and increased hydrogen storage materials’ instrumentation to perform more than 200 measurements on materials from external sources and more than 1,000 measurements all together.
- The HSCoE dedicated significant effort and made substantial progress on spillover.
 - UM demonstrated that oxygen surface functionalities and adsorbed molecules from gaseous impurities (such as methane) in H_2 can enhance spillover. In addition, UM identified that Ti and V chlorides improve catalysts functions.
 - NREL identified that barriers to migration are lowered sufficiently to enable spillover via structural features, electric perturbations, and/or quantum mechanical tunneling where H will diffuse before it desorbs.
 - NREL developed new catalyst processing that improved spillover capacity and charging rates. This includes the observation that B-substituted receptor materials enhance spillover performance. NREL also identified potential issues that produce irreversibilities and cause irreproducible hydrogen sorption measurements.
 - Rice calculated that B and N provide good anchors for metal spillover catalysts, and that N-doping may enhance spillover kinetics. Furthermore, Rice calculated that the barrier for H to move from the metal catalyst to the hydrogenated phase is very small and can be overcome at room temperature.
 - Caltech synthesized 3-gm batches of Pt-loaded super-activated carbon for spillover analyses. Caltech investigated the effect of sample size on the measurements to observe spillover and concluded that some of the inconsistencies in the data may be related to small sample sizes.
- The HSCoE synthesized and characterized several types of new, promising hydrogen sorption materials.
 - ANL and University of Chicago synthesized and characterized over 50 different structures in three classes of polymers. Polymers with specific surface areas as high as $\sim 1,900 \text{ m}^2/\text{g}$ and tunable pore size from 0.6 to 0.9 nm were prepared. Excess H_2 sorption of 5.1 wt% at 77 K (40 bar) and material bulk densities of $\sim 1.4 \text{ g/ml}$ were achieved with virtually no loss in storage capacity.
 - Caltech synthesized intercalated graphite materials that maintain constant isosteric heats of adsorption for their entire capacity range. The isosteric heat in KC24, RbC24, and CsC24 is 9, 11, and 13 kJ/mole H_2 , respectively, and unlike most other physisorbents where the heats decay as a function of loading, the values from intercalated graphites are generally constant as a function of loading.

- Texas A&M University synthesized 50 new ligands for MOF formation and evaluated the contribution to hydrogen adsorption from catenation in MOFs. Also, the effect of a variety of MOF open metal centers and double-bond-containing ligands on hydrogen affinity was studied. In addition, TAMU discovered a general way to construct MOFs by incorporating mesocavities with microwindows to create materials with extremely high specific surface areas. Materials with the highest specific surface areas ever produced (over 9,000 m²/g) were synthesized.
- LLNL worked in collaboration with Metal Hydride Center of Excellence members at HRL Laboratories to develop novel carbon aerogels with large pore volumes and containing dispersions of carbon nanotubes as scaffolds for CA/LiBH₄ nanocomposites. These materials showed a decrease in hydrogen desorption temperature relative to bulk LiBH₄. In addition, aerogels containing functional groups capable of binding and stabilizing organometallic species were synthesized to provide absorption sites for single-metal centers that provided enhanced dihydrogen binding.
- Duke developed thermal treatments of PEEK materials with high specific surface areas (>3,000 m²/g), high microporosity, higher binding energy (8.1 kJ/mol), and >6 wt% at 77 K, 20 bar with a projected 42g/L volumetric capacity. Complementary H₂-NMR measurements showed >6 wt% storage at 120 K and 10 MPa. Also developed methods for successfully doping these high-surface-area porous carbons with variable amounts of B and Pd.
- PSU and NREL demonstrated that incorporation of boron into nanoporous carbon frameworks improve isosteric heats of adsorption for hydrogen to 11–15 kJ/mol and were able to increase boron concentrations in porous materials to ~15%. In addition, boron-substituted carbon demonstrated improved metal integration for stronger dihydrogen storage as well as improved spillover. The enhanced binding energy is sufficient to store substantial hydrogen within the DOE target temperature range of ~220 to 350 K.
- NREL developed novel, scalable, synthetic processes, such as templating, to form high-surface-area lightweight materials with optimum pore structure and composition for H₂ storage. This included the ability to form BC_x materials that have shown great promise for stabilizing single-metal centers for enhanced dihydrogen storage and for improving metal catalysts for spillover.
- ORNL synthesized SWNHs with tunable small pores in gram quantities, which is a scalable production rate. Short, opened SWNHs reversibly store significant hydrogen at room temperature (1.5 wt% at 100 bar). These “nanoengineered pores” are defined by both the unique nanostructure self-assembled during synthesis and the activated pores during oxidation.
- ORNL developed methods to produce uniformly vapor-deposited Ca to attempt to form enhanced binding due to induced charge separation. Theoretical predictions suggest that Ca and Sr should coat C nanostructures without clustering while providing sufficient electric field strength to polarize and bind H₂ with 8.4 wt% and 0.4 eV for Ca.
- Rice produced graphene-nanoribbon scaffolds as H₂ storage slit-pore materials using scalable industrial-type spinning processes. In addition, a dynamic multilayer adsorption concept using electrostatic enhancement for H₂ storage was investigated.
- APCI enhanced its experimental capabilities to allow the use of pure fluorine for the synthesis of graphene-intercalated compounds. First-stage graphene-intercalated compounds containing fluoride anions were prepared using pure F₂ and were characterized for hydrogen storage capacity and heat of adsorption. In addition, new synthetic strategies for the preparation of high-surface-area, templated, boron-substituted carbons were developed.
- On top of those already mentioned, the HSCoE made several important accomplishments in the area of theory and modeling.
 - At APCI, predictive computational modeling revealed that crystalline BC₃ is an attractive target material for hydrogen storage. Unlike graphite, chemisorption of hydrogen by BC₃ provides a chemical driving force for H₂ penetration into the lattice. The energies of hydrogen diffusion of chemisorbed hydrogen in BC₃ were calculated, showing that hydrogen diffusion on the surface is unlikely at moderate temperatures. Although the bond dissociation energies of chemisorbed hydrogen in BC₃ suggest that hydrogen binding may be irreversible at high levels of hydrogenation, APCI's computational modeling suggests a path forward by incorporating substitutional nitrogen atoms in the lattice. The average absorption energies for materials that incorporate nitrogen are significantly lower.
 - At NREL, theory and experiment continued to iteratively interact to design and synthesize

several new H₂ storage materials. This included validating the initial theoretical prediction to experimental Ti-silica results from the University of Windsor of single-metal atoms dispersed and stably supported on a matrix being able to reversibly hold more than 2 H₂. These calculations also revealed the unique properties of inexpensive Ca to make hydrogen storage materials with very viable synthetic routes. These revolutionary new Ca materials could store H₂ at >100 g/L and >10 wt% (much higher than liquid hydrogen) at ambient temperatures, offering the potential to exceed DOE's ultimate system targets including cost and volumetric/gravimetric capacities.

- Rice performed Grand Canonical Monte Carlo simulations to optimize the storage in 3-dimensional foams. The specific surface areas of foams were evaluated and quantum corrections were incorporated to estimate realistic storage capacities. Hydrogen uptakes in metallacarboranes were also studied.

Introduction

To realize the full energy efficiency, energy savings, and environmental improvements that fuel cells can provide, significant improvements over currently available gas storage technologies are required. The storage targets presented in DOE's Multi-year Research, Development and Demonstration Plan for Fuel Cell Technologies state the critical needs and goals. At this time, no known storage system can meet the mass, volume, cost, safety, and efficiency requirements for vehicular or early market storage systems. Consequently, DOE is investigating solid-state storage options such as metal hydrides, chemical hydrides, and sorbent materials. Nanostructured high-surface-area materials containing carbon, metals, oxygen, and other elements show tremendous promise for breakthrough performance in gas storage. However, the capabilities of these materials can be improved by developing a better understanding of both the factors governing their performance and the design principles for synthesizing the materials and constructing the required systems.

The HSCoE is developing reversible sorbent materials for energy storage within the U.S. DOE Fuel Cells Technology Project. The HSCoE is developing the science base and technology advances required to meet DOE goals for on-board storage by researching a range of nanostructured adsorbents. A guiding principle in developing the required material is that a continuum of energies exists for binding to substrates and molecules. On the weak side of the continuum is non-dissociative physisorption due purely to van der

Waals (vdW) forces (4 kJ/mol). On the strong side is the full chemical bond in materials such as methane (with an energy of ~400 kJ/mol). Between these two limits, with binding energies between 10 and 50 kJ/mol, are: (i) stronger physisorption (due to modification of the key parameters affecting vdW forces), (ii) dihydrogen binding via the formation of complexes that exhibit bond stretching and joint charge transfer interactions, and (iii) weak, reversible chemical bonding of mono-atomic hydrogen to strained receptor materials ("spillover"). The DOE goals can be met with sorption-based materials if (i) the energy for adsorption can be designed to be in an optimal range (10–50 kJ/mol) [1], and (ii) efficient volumetric arrangement of a sufficient number of suitable binding sites can be achieved with a low-weight material. These goals are difficult to reach in conventional high-surface-area adsorbents that are limited by low physisorption binding energies, heterogeneity of the adsorbent surfaces and adsorption sites, and excessive macroporosity and poor volumetric packing.

Approach

The main goals of the HSCoE are to discover the limits of performance of high-surface-area adsorbents and to synthesize and test sorbents that can be used to meet the DOE system targets for reversible storage. This involves the design and synthesis of materials that bind large amounts of hydrogen on both a per-weight and a per-volume basis as (i) weakly and reversibly bound atoms and/or (ii) strongly bound molecules. The HSCoE focuses on determining binding mechanisms and energies, and the manner in which suitable sites may be organized in space to achieve a high-volumetric density using low-weight frameworks. This involves determining the affects of geometry, introduction of defects, adventitious dopants, and catalytic species, as well as elemental substitution. The HSCoE currently investigates a range of different lightweight nanomaterials and porous frameworks. In addition to the current materials systems being studied, the HSCoE strives to be nimble, flexible, and responsive to incorporating promising new ideas, materials, and concepts as they arise.

Results

HSCoE members work closely together to effectively leverage unique partner capabilities in a coordinated set of focused efforts to accelerate storage materials development. This close and actively coordinated interaction has resulted in more than 40 joint projects in the past year, in which the rapid materials development is illustrated by the more than 30 joint publications. In addition, the HSCoE works with more than 40 groups from around the world and directly with the chemical hydride and metal hydride centers of excellence to

ensure that our development efforts leverage other research activities for efficient utilization of resources. Finally, the HSCoE also ensures that its development efforts are transparent and provided to the scientific community in a timely manner to again help speed the storage materials' development progress. This is done through the active organization by HSCoE partners of hydrogen storage materials conferences around the world, and through more than 110 presentations at conferences and more than 90 publications in refereed journals in the past year. A few highlights of results from the massive amount of development work from throughout the HSCoE are provided below.

Optimizing High-Specific-Surface-Area Materials

In general, storage capacities increase with higher specific surface areas and higher bulk densities. However, while these are necessary requirements for high storage capacities, enhanced binding energies for the entire capacity range will be required in order for the materials to be used to meet DOE targets. The HSCoE has focused efforts to improve all of these material properties independently and simultaneously. Recently, a tremendous amount of progress has been made on increasing specific surface areas of materials using coordinated framework and porous carbon materials. Material capacities of ~ 7 wt% have been demonstrated. The HSCoE is pursuing a number of different synthetic routes to form optimized geometric materials using processes that include: templating, graphene, aerogel, chemical, vapor, and/or pyrolysis. Even though most of these materials will require cryocompression, they have no significant heat transport issues, can operate at moderate pressures, and may require the least engineering (compared to metal or chemical hydrides) to design and construct a system that could meet the DOE 2010 targets.

Within the HSCoE this year, Hongcai Zhou's group at TAMU developed a number of MOFs with record amounts of specific surface area, including one with over $9,000 \text{ m}^2/\text{g}$ (Langmuir). These materials have yet to be characterized for their hydrogen storage properties, but the interconnected matrix used to form these materials offers the potential for better optimized pore sizes, as compared to other MOF materials. Furthermore, Di-Jia Liu's group at ANL demonstrated that, unlike heterogeneous pore size materials (e.g., activated carbon), their polymer materials with small (i.e., less than 1 nm) uniform pore sizes can be compressed to form materials with $\sim 1.4 \text{ g/ml}$ bulk densities without significant loss of gravimetric hydrogen storage capacity. As shown in Figure 1, if bulk densities close to this can be achieved with 6 to 7 wt% hydrogen storage materials, then volumetric capacities surpassing those of liquid nitrogen (i.e., 70 g/L) could be achieved at a much higher temperature. This will dramatically reduce

system and delivery costs. Finally, Channing Ahn's group at Caltech synthesized stage I intercalated graphite structures (Figure 2) to demonstrate that materials with uniform and small (i.e., 0.5 to 0.6 nm) pore size or wall spacing result in binding energies that remained constant for the full capacity range. These results also demonstrate clearly that smaller spaces increase binding energy, with $\sim 13 \text{ kJ/mol}$ being observed for Cs

FIGURE 1. Plot of the volumetric-capacity dependence on material density and gravimetric capacity.

FIGURE 2. Schematic of stage I intercalated graphite materials and the measured binding energies of K-intercalated graphite, which stays constant for the entire range of capacity.

intercalated graphite. The experimental data indicate that at this binding energy, a substantial amount of the capacity still remains at ~200 K. All of these noteworthy results from the HSCoE partners demonstrate viable pathways to creating sorbent materials that may operate at cryocompressed conditions, but may be used to meet DOE targets.

Improving Site-Specific Dihydrogen Binding Energy

In addition to optimizing geometric structures to improve storage properties, the HSCoE has pioneered the use of multiple-element materials to improve dihydrogen binding. In good agreement with theoretical models [2], B substituted with an sp^2 structure in carbon enhances hydrogen binding to ~11 kJ/mol [3]. The main issues remaining include the need to substantially increase the B concentration while maintaining a high specific surface area (see PSU and NREL contributions to this report). In this regard, the HSCoE is investigating the use of several synthetic techniques to address these issues, including: pyrolysis of BC precursor materials, templating BC_3 , and chemical replacement processes. Similarly, APCI (see their contribution in this report) is investigating the use of F to enhance dihydrogen binding.

In addition to B enhancing dihydrogen binding and thus storage capacity at near-ambient temperatures, B and N have also been used to stabilize single-metal centers and metal clusters on high-surface-area materials. NREL has championed the use of coordinated metal centers to increase dihydrogen binding and to also enable multiple dihydrogen binding at a single adsorption site. Furthermore, some of these materials bind dihydrogen in the optimized range for the entire capacity (Figure 3), which decreases the engineering required while increasing the total storage capacity. Although initial reaction to these materials was skeptical, recent experimental results validate the predictions, and there is good agreement between the predictions and all known 3-d metal center materials. Recently, substantial amounts of work identified the unique properties of Ca for hydrogen storage [4,5]. ORNL's work indicates that the interactions between Ca and carbon matrices is sufficient to prevent Ca agglomeration; enabling single metal atoms to be maintained for multiple dihydrogen adsorption at each Ca atom. As discussed in the NREL contribution to this report, Ca coordinated in the correct way can reversibly store over 100 g/L and 10 wt% at ambient temperatures (Figure 4). This is substantially higher than liquid hydrogen, but at ambient temperature. Based on initial calculations from ANL, storage systems at ~75% of the material capacities should be achievable under these conditions. Thus, these inexpensive Ca-based hydrogen storage materials provide a reasonable path for meeting DOE's ultimate storage targets (i.e., 7.5 wt% and 70 g/L).

FIGURE 3. Some coordinated metal center materials maintain optimum hydrogen binding energies for their entire capacity range. This helps engineering and enhances the material capacity.

FIGURE 4. Plots of predicted material capacities for different coordinated metal materials. Ca-based materials have the potential to exceed all of them and to be used to meet DOE's ultimate targets.

Improving Spillover Material Processing

While most of the work within the HSCoE is associated with enhancing the storage of molecular hydrogen, we are also developing materials that can reversibly store weakly bound hydrogen atoms. For example, Ralph Yang's group at the University of Michigan pioneered the use of spillover as a viable high capacity ambient temperature hydrogen storage process. UM demonstrated that over 4 wt% hydrogen can be reversibly stored on a catalyst containing MOF material, and calculations indicate that 7–8 wt% (50–60 g/L) should be achievable at ambient temperature. In addition, analysis from ANL indicate that systems using spillover materials could have ~75%

of the material capacities, suggesting that the DOE 2015 targets of 5.5 wt% and 40 g/L could be achieved with an optimized spillover material. Thus, the HSCoE has several partners including UM investigating the different components of spillover and improving materials synthesis to resolve the remaining issues associated with reproducibilities, capacities, refill rates, and costs. Initial work validated the thermodynamics of the spillover processes and broadened the breadth of materials that demonstrate spillover. In the past year, work at NREL and Rice University developed a better understanding of how the hydrogen moves from the catalyst to the receptor and then also along the receptor. With this understanding, the HSCoE can guide development efforts to improve material performance further. In addition, UM and NREL identified a number of ways to improve catalytic and receptor material performance. However, NREL also identified several issues that contribute to batch-to-batch and lab-to-lab irreproducibilities in the materials processing, and the fact that the effluent gas needs to be actively monitored to ensure that undesired chemical reactions with surface functional groups is not occurring.

Conclusions

- The HSCoE partners worked closely together to systematically accelerate the development of advanced hydrogen sorbent materials. This resulted in the development of multiple new materials that may meet the 2010 DOE storage system targets including cost and gravimetric/volumetric capacities.
- Designed/developed substituted materials to enable higher hydrogen binding energies in porous materials. Demonstrated higher B concentration (10%–15%) in carbon with higher surface areas (800 m²/g). BC_x materials could increase the storage tank temperature and capacity, thus reducing overall system costs.
- Developed new materials with stronger H₂ binding either through interactions with exposed metal centers or electrostatic effects. This work paves the way to meet DOE's ultimate storage targets with ambient temperature storage densities greater than liquid H₂.
- Identified new material processes that increase sorption rates and hydrogen storage capacity by >15% at room temperature.
- Improved spillover kinetics understanding enables materials to be designed with higher capacities and sorption rates that can meet DOE 2015 targets. Identification of hole-induced improvements along with receptor catalytic properties points toward inexpensive spillover material with fast sorption.
- HSCoE has dozens of collaborative interactions that are openly discussed, evaluated, and redirected during face-to-face meetings and with Webcasts either in small groups or by the whole center.
- HSCoE works with dozens of groups and provides leadership throughout the world.

Future Directions

- **Focused Materials Development:** Wrap up focused materials development work and complete materials characterization and validation. Maintain awareness of advances made in different focused development efforts and other groups, to ensure efficient coordination of efforts.
 - **Porous materials:** Develop high-surface-area materials with optimized pore structure for efficient volumetric capacities and enhanced hydrogen binding. Integrate substituted elements (e.g., boron in porous carbons) produced by scalable processing (e.g., templates, propped graphenes, carbon and non-carbon aerogels). Work interactively to characterize the structural properties, analyze the optimal pore effect, and investigate the highest potential for H storage for different sorption mechanisms. Leverage carbon-based materials' experience to determine if other light elements can be used to implement mechanisms more straightforwardly, or if brand new, more desirable approaches may be found.
 - **MOF Materials:** Further enhance H₂-MOF interactions by preparing materials with a higher density of coordinatively unsaturated metal centers, improve H₂ uptake at temperatures higher than 77 K by ligand and MOF design, and increase MOF thermal stability while maintaining its porosity. Increase volumetric performance using denser H₂ packing and optimal pore sizes.
 - **Metal-Decorated Structures:** Focus on tractable processing with identification of atomic structures, characterize the reactions, simulate their H-storage properties, and improve the properties.
 - **Spillover Materials:** Work in well-coordinated groups to develop improved understanding of spillover processes and reproducible materials processing. This includes determining the contributions of bridges and receptors to kinetic limitations, thermodynamically acceptable configurations, and the roll catalyst/receptor integration plays. Also, scale materials processing to the multiple (tens)-gram scale for validation and system testing. Perform very high-pressure measurements (>100 bar) to determine saturation capacities.
 - **Integrate Theory and Experiment:** Iterative, close interactions in the HSCoE have

already taught theoreticians what is possible experimentally, and *vice versa*. Continued work at this interface will increase the rate of discovery and synthesis of viable materials.

- **Materials Down-Select:** After down-selecting, allocate resources focused on completing work on selected materials to demonstrate their potential to meet DOE 2010 and 2015 system targets and to provide performance properties for system design. Also, identify potential cost-effective and scalable processing that will produce the hydrogen storage materials with access to the high density of enhanced binding energy sites.
- **Provide Recommendations:** Provide DOE with a comprehensive review of all significant work done, results, lessons learned, and recommendations for future sorption materials development in a report and publication. Key aspects of this review will include material and/or process recommendations for future consideration in engineering system analysis, design, and demonstration, as well as future research and development efforts.
- **Support HSECoE:** Work with the HSECoE to select potential materials and provide their intrinsic hydrogen storage properties needed for system engineering design, analysis, and perhaps demonstration.
- **Sorbent Materials Approach to DOE 2010 Targets:** In general, sorbents meet almost all of the DOE hydrogen storage targets. As discussed above, sorbents may greatly improve volumetric capacities, and the HSECoE has developed several materials that may meet DOE's 2010 on-board refueling targets.

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IV.C.1b A Biomimetic Approach to Metal-Organic Frameworks with High H₂ Uptake

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Objectives

- Design, synthesis, and characterize high-surface-area metal-organic frameworks (MOFs) with active metal centers aligned in porous channels and accessible by H₂ molecules.
- Through optimized, cooperative binding, the MOFs are expected to have enhanced affinity to H₂.
- These MOFs can help to reach the DOE 2010 and ultimately 2015 hydrogen storage goal.

Technical Barriers

This project addresses the following technical barriers from the Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (P) Lack of Understanding of Hydrogen Physisorption and Chemisorption
- (Q) Reproducibility of Performance

Technical Targets

- The focus of the proposed research is the use of concepts evident in metalloproteins to guide the synthesis of MOFs with gas-adsorption affinity around 15 to 20 kJ/mol for hydrogen and high surface area.

- The overall objective is to achieve the DOE 2010 and 2015 system goals, primarily the gravimetric and volumetric storage goals, at or near ambient temperatures and moderate pressure for on-board vehicular hydrogen storage (Table 1).

Accomplishments

- Synthesized 50 new ligands for MOF formation.
- Evaluated the contribution to hydrogen adsorption from catenation in MOFs.
- Studied the effect of a variety of open metal centers on hydrogen affinity of the MOFs.
- Explored double-bond containing ligand and its influence on hydrogen adsorption.
- Discovered a general way toward MOFs with extremely high surface area: incorporation of mesocavities with microwindows.

TABLE 1. System Targets: On-Board Hydrogen Storage for Light-Duty Vehicles

Storage Capacity	Units	2010	2015	Ultimate	Texas A&M (excess, sorbent-based)	
Gravimetric: net useful H ₂ /max system mass	kg H ₂ /kg system	0.045	0.055	0.075	0.072 77 K, 50 bar	0.009 298 K, 50 bar
Volumetric: net useful H ₂ /max system volume	kg H ₂ /L system	0.028	0.040	0.070	0.040 77 K, 50 bar	0.005 298 K, 50 bar

Introduction

In the past decade, there has been an escalation of interest in the study of MOFs due to their fascinating structures and intriguing application potential. Their exceptionally high surface areas, uniform yet tunable pore sizes, and well-defined adsorbate-MOF interaction sites make them suitable for hydrogen storage. Various strategies to increase the hydrogen capacity of MOFs, such as using pore size comparable to hydrogen molecules, increasing surface area and pore volume, utilizing catenation, and introducing coordinatively unsaturated metal centers (UMCs) have been widely explored to increase the hydrogen uptake of the

MOFs. Recently, inelastic neutron scattering (INS) and neutron powder diffraction as well as computational studies suggest that the choice of both metal centers and ligands can play an important role in tailoring the gas-framework interactions. Additionally, those ligands containing phenyl rings have been proven favorable for hydrogen adsorption. MOFs with hydrogen uptake approaching the DOE 2010 gravimetric storage goal under reasonable pressure but cryo-temperature (typically 77 K) were reported. However, the weak interaction between hydrogen molecules and MOFs has been the major hurdle limiting the hydrogen uptake of MOFs at ambient temperature.

Approach

Our strategy to enhance H_2 uptake was as follows: (1) Prepared the catenation isomer pair to evaluate the contribution from catenation to the hydrogen uptake of a MOF material. (2) Synthesized porous MOFs with high hydrogen adsorption affinities based on different coordinatively UMCs. (3) Hydrogen storage studies in MOFs containing nanoscopic cages based on double-bond-coupled di-isophthalate linkers. (4) Obtained stable MOFs with high surface areas by the incorporation of mesocavities with microwindows.

Results

In the past year, we have prepared a series of MOFs and explored their applications in hydrogen storage. Table 2 shows the comparison of hydrogen uptakes of selected MOFs. Next we will discuss in detail the results of H_2 uptakes of these MOFs.

(a) Catenation Isomer Pair of MOFs

Catenation, the intergrowth of two or more identical frameworks, has long been an interesting topic in MOF research. It can be utilized as an alternative way to reduce pore sizes in porous MOFs and has also been explored as an efficient method to improve the hydrogen uptake of MOFs. Recently, we developed a templating strategy to control catenation/noncatenation in porous MOFs, obtained the catenation isomer pair of PCN-6 and PCN-6', and were able to quantitatively evaluate the contribution from catenation to the hydrogen uptake of a MOF material (Figure 1). Our studies revealed that catenation can lead to a 41% improvement of apparent Langmuir surface area (3,800 m^2/g for PCN-6 vs 2,700 m^2/g for PCN-6'), a 29% increase in excess gravimetric hydrogen uptake (1.74 wt% for PCN-6 vs 1.35 wt% for PCN-6') at 77 K/760 torr, and a 133% increase in volumetric hydrogen uptake (9.19 kg/m^3 for PCN-6 vs 3.49 kg/m^3 for PCN-6') in the catenation isomer pair of PCN-6/PCN-6'. The study of isosteric heats of adsorption indicated that catenated PCN-6

and noncatenated PCN-6' have similar hydrogen-adsorption enthalpies at low coverage (6.2 kJ/mol for PCN-6 vs 6.0 kJ/mol for PCN-6'). However, as the hydrogen loading increases, PCN-6 exhibits steadily higher hydrogen-adsorption enthalpies than those of PCN-6'. INS spectroscopy studies revealed that the first sites occupied by H_2 are the open Cu centers of the paddlewheel units in both PCN-6 and PCN-6'. However, in PCN-6, there exist three specific H_2 -binding Cu sites while PCN-6' possesses only one. At high hydrogen loadings, the interaction between H_2 molecules and the organic linkers is stronger in catenated PCN-6 than that in noncatenated PCN-6'. Such a stronger interaction resulted in more effective hydrogen binding sites in catenated PCN-6. Hydrogen sorption studies up to 50 bar demonstrated that catenation can lead to higher hydrogen uptake in MOFs even at high pressure. For example, the excess hydrogen uptake of catenated PCN-6 is 72 mg/g (6.7 wt%) at 77 K/50 bar or 9.3 mg/g (0.92 wt%) at 298 K/50 bar, and that in noncatenated PCN-6' is 42 mg/g (4.0 wt%) at 77 K/50 bar or 4.0 mg/g (0.40 wt%) at 298 K/50 bar. Importantly, PCN-6 exhibits a total hydrogen uptake of 95 mg/g (8.7 wt%) (corresponding to 53.0 g/L) at 77 K/50 bar and 15 mg/g (1.5 wt%) 298 K/50 bar. Significantly, the deliverable (50 to 1.5 bar) hydrogen capacity of PCN-6 is 75 mg/g (or 41.9 g/L) at 77 K/50 bar, showing its great potential as a cryogenic hydrogen-storage medium.

TABLE 2. Comparison of Hydrogen Uptakes of Selected MOFs

Material	ΔH_{ads} (kJ/mol)	H_2 Adsorption			
		Gravimetric H_2 uptake (wt%)	Volumetric H_2 uptake (g/L)	T (K)	P (bar)
PCN-6	6.2~4.5	7.2	40.2	77	50
		1.90	10.6	77	1.0
		0.92	5.14	298	50
PCN-6'	6.0~3.9	4.2	11.8	77	50
		1.62	4.73	77	1
		0.40	1.12	298	50
(Co) PCN-9 (Fe) (Mn)	10.1	1.53	14.1	77	1
	6.4	1.06	9.60	77	1
	8.7	1.26	11.3	77	1
PCN-61	9.3~4.5	4.28	14.8	77	16
		2.11	7.32	77	1
		0.65	2.25	298	109
PCN-66	7.2~4.5	1.69	4.26	77	1

(b) Porous MOFs with Different UMCs

The implementation of coordinatively UMCs into porous MOFs has been considered one of the most attractive ways to improve their affinities to hydrogen. Recent theoretical calculations suggested that the H_2 -open metal center interactions may be tuned by

FIGURE 1. (a) The framework of catenated PCN-6. (b) The framework of noncatenated PCN-6'. (c) Excess hydrogen sorption isotherms of PCN-6 and PCN-6' at 77 (red) and 298 K (black): circles, PCN-6; squares, PCN-6'; solid symbols, adsorption; open symbols, desorption. (d) Isothermic heats of adsorption for PCN-6 and PCN-6'.

varying the metal types, and the evaluation of different UMCs' affinities to hydrogen molecules will be very instructive for the future design of porous MOFs with high hydrogen adsorption capacities, especially at near ambient temperatures. Herein, we prepared three isostructural porous MOFs, designated as PCN-9 (Co), PCN-9 (Fe) and PCN-9 (Mn), respectively. To test the permanent porosities of the three porous MOFs, N_2 sorption isotherms were measured at 77 K. All of them exhibit type-I sorption behavior, as expected for microporous materials. Derived from the N_2 sorption data, the Brunauer-Emmett-Teller (BET) surface areas are 1,064 m^2/g (Langmuir surface area, 1,355 m^2/g), 682 m^2/g (Langmuir surface area, 848 m^2/g), and 836 m^2/g (Langmuir surface area, 1,057 m^2/g) for PCN-9 (Co), PCN-9 (Fe), and PCN-9 (Mn), respectively. H_2 sorption measurements at 77 K were also carried out to check their hydrogen storage performances. At 77 K and 760 Torr, the hydrogen uptake capacity of PCN-9 (Co) is 1.53 wt%, and PCN-9 (Fe) can adsorb 1.06 wt% hydrogen, while PCN-9 (Mn) can uptake 1.26 wt% hydrogen. The H_2 affinities of the three porous MOFs have been estimated by isosteric heats of adsorption (Q_{st}). PCN-9 (Co) has a Q_{st} of 10.1 kJ/mol and PCN-9 (Mn) has a Q_{st} of 8.7 kJ/mol, while PCN-9 (Fe) has a relatively lower Q_{st} of 6.4 kJ/mol. These results revealed that the Co UMC possesses a higher hydrogen affinity

compared to the Fe and Mn UMCs, indicating that the implementation of open Co centers into porous MOFs may be a promising way to enhance hydrogen adsorption enthalpies for near-ambient hydrogen storage application.

(c) MOFs Based on Double-Bond-Coupled Di-Isophthalate Linkers

While ligands containing phenyl rings have been proven favorable for hydrogen adsorption, those containing double-bond functionalities have rarely been studied in gas adsorption MOFs. Herein, we present hydrogen storage studies in MOFs containing nanoscopic cages based on two predesigned double-bond-coupled bis(isophthalate) ligands: azobenzene-3,3',5,5'-tetracarboxylate (abtc) and transstilbene-3,3',5,5'-tetracarboxylate (sbtc). Solvothermal reactions of $Cu(NO_3)_2$ with H_4abtc or H_4sbtc give rise to isostructural PCN-10 and PCN-11, respectively. The enduring porosity of PCN-10 and PCN-11 is confirmed by gas adsorption studies. The N_2 adsorption isotherms of the activated samples exhibit type-I sorption behavior with a Langmuir surface area of 1,779 or 2442 m^2/g , corresponding to

a BET surface area of 1,407 or 1,931 m^2/g and a total pore volume of 0.67 or 0.91 mL/g for PCN-10 or PCN-11, respectively. In particular, both contain nanoscopic cages that are particularly suitable for gas storage. At 760 Torr and 77 K, the excess hydrogen uptake of PCN-10 is 2.34 wt% (18.0 g/L) and that of PCN-11 is as high as 2.55 wt% (19.1 g/L). When the pressure is increased, the excess adsorption at 77 K saturates around 20 atm and reaches values of 4.33% (33.2 g/L) and 5.05% (37.8 g/L) for PCN-10 and PCN-11, respectively. Gas adsorption experiments suggest that MOFs containing C=C double bonds are more favorable than those with N=N double bonds in retaining enduring porosity after thermal activation, although the N=N double bond has slightly higher H_2 affinity.

(d) MOFs with the Incorporation of Mesocavities and Microwindows

Polyhedron-based MOFs may lead to higher stability and porosity if the sizes of the open windows of the polyhedra are limited. Herein we report a strategy for stabilizing MOFs with high surface areas by introducing mesocavities with microwindows into the MOFs based on the (3,24)-connected network. The nanoscopic hexatopic carboxylate

FIGURE 2. (a) Nanoscopic ligand btei and cuboctahedra as structural building units in PCN-61. (b) Nanoscopic ligand ntei and cuboctahedra as structural building units in PCN-66. (c) N_2 sorption isotherms for PCN-61 (black) and PCN-66 (red) at 77 K. Filled and open circles represent adsorption and desorption data, respectively.

ligands designed for this purpose are 5,5',5''-benzene-1,3,5-triyltris(1-ethynyl-2-isophthalate) (btei) and 5,5',5''-(4,4',4''-nitrilotris(benzene-4,1-diyl)tris(ethyne-2,1-diyl))triisophthalate (ntei) and solvothermal reactions of H_6 btei and H_6 ntei with copper salts yielded two MOFs, PCN-61 and PCN-66 (Figure 2). With the BET model, an activated PCN-61 sample was estimated to have a specific surface area of $3,000 \text{ m}^2 \text{ g}^{-1}$, and the Langmuir surface area was $3,500 \text{ m}^2 \text{ g}^{-1}$ assuming monolayer coverage. For PCN-66, where the larger ligand was used, there was a remarkable increase in surface area (BET, $4,000 \text{ m}^2 \text{ g}^{-1}$ and Langmuir, $4,600 \text{ m}^2 \text{ g}^{-1}$), which supports our hypothesis that the expansion of the ligand leads to increased surface area. To the best of our knowledge, PCN-66 possesses the highest surface area reported to date for MOFs based on paddlewheel clusters. It can be extrapolated that use of even larger hexatopic carboxylate ligands may lead to stable MOFs with even higher surface areas. The high surface area in PCN-61 and PCN-66 prompted us to evaluate their hydrogen adsorption performance. At 77 K and 760 Torr, the excess gravimetric hydrogen uptake capacity of PCN-61 and PCN-66 can reach 2.11 wt% (corresponding to 7.32 g/L) and 1.69 wt% (corresponding to 4.26 g/L), respectively. At higher pressure, the excess hydrogen uptake of PCN-61 is 4.28 wt% (corresponding to 14.8 g/L) at 77 K/16 bar or 0.65 wt% (corresponding to 2.25 g/L) at 298 K/50 bar. The high pressure hydrogen adsorption studies of PCN-66 are currently underway and will be reported next year.

Conclusions and Future Directions

Conclusions

- MOFs containing catenation possess high capacity of hydrogen adsorption.
- MOFs containing UMCs tend to have high hydrogen affinity; MOFs based on different UMCs show different hydrogen adsorption capacities.
- MOFs containing nanoscopic cages based on double-bond-coupled di-isophthalate linkers have been proven favorable for hydrogen adsorption.
- MOFs with the incorporation of mesocavities and microwindows exhibit high surface areas and good potential in hydrogen storage.

Future Directions

- Further enhancement of H_2 -MOF interaction by the introduction of higher density of coordinatively UMCs (heat of adsorption 15 kJ/mol).
- Improvement of H_2 uptake at temperatures higher than 77 K by ligand and MOF design.
- Increase MOF thermal stability while maintaining its porosity.
- Preparation of MOFs with high surface area and optimized cage size ($6,000 \text{ m}^2/\text{g}$).

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IV.C.1c Hydrogen Storage by Spillover

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- To modify carbon (e.g. by oxidation) to increase spillover storage.
- To develop and optimize our new bridge-building techniques for spillover to enhance hydrogen storage.
- To develop direct metal doping technique on carbons for maximum spillover storage.
- To develop synthesis methods for ultrahigh surface area carbons ($>3,500 \text{ m}^2/\text{g}$).
- To obtain a mechanistic understanding for hydrogen spillover in nanostructured materials for hydrogen storage

Accomplishments

- Demonstrated that adsorbed gas molecules, from gaseous impurities (such as methane) in H_2 , can serve as bridges for spillover thereby increase spillover-storage by $>15 \text{ wt}\%$.
- Showed that oxygen surface functionalities on carbon can increase spillover storage on carbon, by a factor of three.
- A class of catalysts has been found for increasing spillover rates - in both directions.
- Showed that spillover-storage is potentially capable of meeting DOE system targets (at ambient temperature).

Objectives

- This project is/was working towards the former 2010 system targets including capacity targets of 6 percent hydrogen by weight and 45 grams hydrogen per liter.
- To develop new sorbents to achieve the DOE targets by using nanostructured carbons or other sorbents such as metal organic frameworks (MOFs) aided by hydrogen spillover.
- To develop a mechanistic understanding for hydrogen spillover that leads to hydrogen storage.

Technical Barriers

- General barriers: gravimetric and volumetric storage capacities.
- Rates: uptake rate only (discharge rate exceeds DOE target).
- Lack of understanding for hydrogen spillover.

Technical Targets

To develop hydrogen storage materials to achieve the DOE 2010 targets (see above) at room temperature:

- To develop new bridging techniques to maximize spillover storage.
- To increase the rates of spillover.

Introduction

Nanostructured carbons have tremendous potential for spillover-storage at ambient temperature. An added and important benefit for carbon is that carbon is much more stable than MOFs and other materials. The theoretical limit for spillover-storage on carbon is $>8 \text{ wt}\%$ for a carbon with a Brunauer-Emmett-Teller (BET) surface area of $4,000 \text{ m}^2/\text{g}$.

The issues to be addressed are: to increase the spillover amounts and to increase the rates of spillover.

Approach

We are using the templating approach to develop ultra-high surface area carbons. Using these carbons, we are developing the most effective metal doping techniques for spillover-storage.

To address the issues above, we are developing the most effective metal-doping technique as well bridging techniques in order to maximize spillover-storage. To further increase spillover storage on carbons, we

are modifying carbon, such as by introducing oxygen functionalities, to increase spillover. We are also developing catalysts to increase the rates of spillover.

Results

In this report, we show the significant increase in spillover by adsorbing an impurity that is commonly found in H_2 such as CH_4 . Clearly, the adsorbed CH_4 molecules serve as bridges for hydrogen spillover. The results also illustrate the significant errors in using the Benson-Boudart method (for estimating the metal dispersion of supported metals) when spillover occurs, particularly that enhanced by gas impurities. All of the adsorbents used in this work were prepared by impregnating a support with chloroplatinic acid (H_2PtCl_6) (Aldrich, 99.9%).

Pt/AX-21: A 6.0 wt% Pt/AX-21 sample was prepared by impregnating H_2PtCl_6 on AX-21 superactivated carbon. The detailed preparation and pretreatment procedures are given in Ref. 4. The BET surface of the AX-21 was $2,880\text{ m}^2/\text{g}$ and that of the Pt/AX-21 was $2,521\text{ m}^2/\text{g}$.

In order to investigate the effect of methane molecules on the spillover of hydrogen from the Pt surface to the AX-21 carbon surface, CH_4 was presorbed at predetermined pressures before H_2 isotherms were measured, as described in the foregoing. The results are shown in Figure 1 and Table 1. Figure 1 shows the effect of CH_4 on hydrogen adsorption. The adsorption capacity of H_2 on Pt/AX-21 varied with the initial pressure of CH_4 . Pre-sorbing with CH_4 in the range of 5.0×10^{-4} to 3.4×10^{-3} atm resulted in significantly increased adsorption of H_2 . From Figure 1 and Table 1, it is seen that the spillover-adsorption amount of H_2 reached the highest value when the initial pressure of CH_4 was at 1.2×10^{-3} atm. At 1.2×10^{-3} atm of CH_4 , the equilibrium adsorption amount of H_2 at 1 atm increased to $8.81\text{ cm}^3/\text{g}$ standard temperature and pressure (STP) from $4.78\text{ cm}^3/\text{g}$ STP without CH_4 , i.e., nearly doubled.

For H_2 storage, high-pressure isotherms were also measured, and the results are shown in Figure 2.

FIGURE 1. Adsorption isotherm of H_2 on Pt/AX-21 at 298 K with presorbed CH_4 at $P(CH_4) = 0$ (●), 5.0×10^{-4} (◇), 1.2×10^{-3} (□) and 3.4×10^{-3} atm (△). The three presorbed CH_4 points fall essentially on the origin due to the large Y-axis scale.

Figure 2 shows that the capacity of pure hydrogen on Pt/AX-21 was 1.20 wt% at 25°C and 100 atm, which was the same with our previous work. The effect of CH_4 on the H_2 storage at high pressures was similar to that at <1 atm. The highest H_2 storage on Pt/AX-21 appeared at 5.0×10^{-3} atm of the initial CH_4 pressure. When the pressure of CH_4 was at 5.0×10^{-3} atm, the H_2 storage reached 1.38 wt%, which was $\sim 15\%$ higher than that of pure H_2 adsorption.

One of the factors determining the spillover-storage amounts is the surface chemistry of the receptor. For carbon, doping by heteroatoms including oxygen may have strong effects. Introducing surface oxygen groups may also have effects. The heteroatom in doped carbon increased the interactions between the receptor and hydrogen, and thus led to enhanced hydrogen adsorption. One may expect therefore, a receptor exhibiting stronger interaction with hydrogen molecules or atoms would be favorable for hydrogen adsorption. In a hydrogen spillover system, the presence

TABLE 1. Results of CH_4 and H_2 adsorption on Pt/AX-21

Initial pressure of PCH_4 (atm)	Saturation Amount of CH_4 (cm^3/g , STP) ^a	Saturation Amount of H_2 (cm^3/g , STP) ^b	Chemisorption Amount of H_2 (cm^3/g , STP) ^c	Platinum Dispersion ^d (%)
0	-	4.78	2.52	73
5.0×10^{-4}	1.5×10^{-2}	7.45	4.92	143
1.2×10^{-3}	3.7×10^{-2}	8.81	5.93	173
3.4×10^{-3}	15×10^{-2}	6.03	3.92	114

^a the saturation amount of CH_4 was obtained at the corresponding initial pressure of CH_4 .

^b the saturation amount of H_2 was obtained at 1.0 atm of H_2 .

^c the chemisorption amounts of H_2 adsorption was obtained at the equilibrium pressure of H_2 extrapolated to zero.

^d dispersion: percentage exposed atoms.

FIGURE 2. Adsorption isotherm of H_2 on Pt/AX-21 at 298 K with presorbed CH_4 at $P(CH_4) = 0$ ($\circ$), 1.0×10^{-3} ($\bullet$), 5.0×10^{-3} ($\blacktriangle$), 1.0×10^{-2} ($\blacksquare$), and 0.1 atm ($\blacklozenge$).

of oxygen groups (as will be shown in our molecular orbital calculations) leads to stronger adsorption for the spillover hydrogen, thus an enhanced storage capacity could be expected on an oxygen modified carbon receptor. Compared with boron or nitrogen doping, addition of surface oxygen groups to a carbon receptor is an easy process. As for direct synthesis, graphite oxide is a well-known carbon material with abundant oxygen groups. By considering these aspects, we prepared two different carbons of super-activated carbon (AX-21) and graphite oxide doped with Pd metals, and investigated the effects of surface oxygen in these carbons on hydrogen storage via spillover.

The following three doped carbons were first prepared (using $NaBH_4$ as the reducing agent): 10 wt% Pd doped on AX-21 (Pd/AX-21), 10 wt% Pd doped on oxygen-modified AX-21 (Pd/AX-21-O), and 10 wt% Pd doped on graphite oxide (Pd/graphite oxide). Elemental analysis by X-ray photon spectroscopy ($O/(C+O)$: w/w) indicated oxygen content in Pd/AX-21-O was about 13 wt%, while that in the graphite oxide was approximately 40 wt%. High-pressure hydrogen isotherms at 298 K for plain AX-21, Pd/AX-21 and Pd/AX-21-O samples are shown in Figure 3. In Figure 3, AX-21 exhibited a hydrogen storage capacity of 0.61 wt% at 298 K and 10 MPa, which is in agreement with previous results. By doping 10 wt% Pd on AX-21 sample, the hydrogen uptakes on Pd/AX-21 and Pd/AX-21-O at 10 MPa were enhanced to 0.98 and 1.15 wt%, respectively. It can be seen that both Pd/AX-21 and Pd/AX-21-O samples exhibited much higher hydrogen adsorption capacities than the plain AX-21 sample. The enhanced hydrogen storage capacity cannot be attributed to the differences in surface area because the doped samples have, in fact, lower surface

FIGURE 3. High-pressure hydrogen isotherms at 298 K for 10% Pd/graphite oxide ($\circ$), 10%Pd/AX-21-O ($\diamond$) and 10% Pd/AX-21 ($\triangle$), normalized by BET surface area. The BET surface areas are: 2,466 m^2/g for Pd/AX-21 and 2,362 m^2/g for Pd/AX-21-O, and 687 m^2/g for Pd/graphite oxide.

areas than plain AX-21, as is evident from nitrogen adsorption results. The enhancement in hydrogen storage was due to the spillover of atomic hydrogen from metal particles to AX-21. The enhanced hydrogen storage by metal-doped on carbon materials have been observed. It is significant that Pd/AX-21-O had a higher storage capacity than Pd/AX-21. Normalized by the BET surface area, the Pd/AX-21-O adsorbed 22% more hydrogen than Pd/AX-21.

In order to increase the rates of spillover, we explored the doping of metal salts to study possible catalytic effects of Ti and V chlorides on hydrogen spillover on Pt-doped carbon. By doping 2 wt% $TiCl_3$ or VCl_3 , the rates for both adsorption and desorption were significantly increased. The H_2 isotherms on the Pt/AX-21 and metal salt doped samples were similar. The rates were expressed in terms of fractional completion vs. time upon each pressure increase step. The results are shown in Figure 4.

Conclusions and Future Directions

Conclusions

- Adsorbed gas molecules, from gaseous impurities (such as methane) in H_2 , can serve as bridges for spillover thereby increase spillover-storage.
- Oxygen surface functionalities on carbon can increase spillover storage on carbon due to higher heats of adsorption.
- A class of catalysts has been found for spillover rates - for both charge and discharge rates.
- Spillover-storage is potentially capable of meeting DOE system targets (at ambient temperature).

FIGURE 4. Rates of adsorption on Pt/AX-21 and Pt/AX-21+TiCl₃ at 25°C and different pressures. Pressure step: (1) 0–6.1 atm H₂ on Pt/AX-21+TiCl₃, (2) 0–5.7 atm H₂ on Pt/AX-21, (3) 6.1–24.0 atm H₂ on Pt/AX-21+TiCl₃ and (4) 5.7–23.5 atm H₂ on Pt/AX-21.

Future Directions

- Develop oxidized carbons for storage by spillover, particularly on graphite oxides with BET surface areas >1,000 m²/g.
- Develop sorbents for storage by spillover with bridge-building on MOFs.
- Obtain a quantitative understanding of kinetics of spillover-storage.
- Develop catalysts for increasing spillover rates for both charge and discharge, and an understanding of catalytic mechanism.
- Develop new direct metal-doping techniques (including plasma treatments) on AX-21 and other ultra-high-surface-area carbons (i.e., templated carbons) with BET surface areas >4,000 m²/g.
- Obtain a basic understanding of the spillover process including equilibrium and kinetics, using deuterium isotope.

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IV.C.1d Optimization of Nano-Carbon Materials for Hydrogen Sorption

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Objectives

- Overall: Model materials structures' interaction with hydrogen, and optimize their makeup for storage and assess the volumetric and gravimetric capacity. Recommend the synthetic goals e.g., pore/channel size, metal enhancement routes.
- Identify obstacles (thermodynamic and kinetic) for the spillover, e.g. metal aggregation, and develop a conceptual model of the process for its improvement.
- Explore doping as an anchor to metal cluster, effect of dopants on spillover threshold.
- Explore the viability of metallacarborane-based metal organic frameworks (MOFs) for enhanced room temperature storage.
- Optimize the volumetric and the gravimetric capacities of the 3-dimensional (3D) foam and suggest the best pore size for the storage.
- Synthesis of metal- and electronegative-group- (F , BF_3) enhanced VANTA (vertically aligned nanotube arrays, *contrast to fibers*) for H_2 adsorption.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section of the

Hydrogen, Fuel Cells and Infrastructure Technologies
Program Multi-Year Research, Development and
Demonstration Plan:

- (A) System Weight and Volume
- (E) Charging/Discharging Rates
- (P) Lack of Understanding of Hydrogen Physisorption

Technical Targets

Carbon-based 3D structures (including metal incorporated structures) for physical and chemi-sorption of hydrogen will be developed. Apply the gained insights towards the design and synthesis of hydrogen storage materials that can meet the DOE hydrogen storage system targets with special emphasis on:

- System Net Gravimetric: 5.5 wt%
- System Volumetric Capacity: 1.3 kWh/L

Accomplishments

- Carried out Grand Canonical Monte Carlo (GCMC) simulations to optimize the storage in 3D foams. The surface areas of foams were evaluated. Quantum corrections were incorporated to estimate realistic storage capacities.
- Hydrogen uptakes in metallacarboranes were studied. Capacities are closer to DOE goals.
- Efforts made towards optimizing the catalysts for spillover. B and N have emerged as good anchors for metal catalysts. N-doping is promising for enhancement of spillover kinetics.
- The barrier for H to move from metal to the hydrogenated phase was found to be very small and can be overcome at room temperature.
- High surface area carbon converted to superacid salts and tested for enhanced hydrogen storage. So far no enhancement of hydrogen storage due to conversion to a superacid has been revealed.

Introduction

The search for novel materials capable of efficiently storing hydrogen for on-board energy use needs guidance from modern materials science, which includes predictive theoretical tools. In this project we combine accurate theoretical models with small-scale pilot synthesis efforts. This activity allows us to provide material design suggestions to the Hydrogen Sorption Center of Excellence partners, as well as to verify selected

experimental approaches in-house. Work done in this project helps the Center to see more promising paths to meeting its goals (e.g., 3D architectures with optimum spacing or enhancement of spillover by introduction of heterogeneous nucleation via bridges), while down-selecting some others which computational analyses do not support as feasible (e.g., densely packed raw single wall nanotube material).

Overall inexpensive 3D foams are designed with optimum porosity for enhanced storage capacity. We have provided a consistent explanation for the spillover process and recognized the key factors (catalyst saturation and improved H-receptor binding energy), which can be modified to improve storage efficiencies. This work will benefit both theoretical and experimental efforts in the center to design efficient catalysts and receptors for spillover. Furthermore, metallacarboranes are proposed as the high storage capacity material, which do not suffer from the clustering of transition metals.

Approach

The modeling approach combines quantum-chemical ab-initio and, wherever possible, classical force fields to achieve the accurate yet affordable predictions of nano-structured systems. GCMC simulations are used, with the judicious choice of interaction potentials, to estimate the storage capacities under ambient conditions. The quantum corrections as suggested by Feynman and Hibbs are included in the potentials. The synthesis approach utilizes novel VANTA growth methods and advances its flexibility towards developing materials best suited for H-storage.

Results

Carbon Foams

We have designed inexpensive carbon foams with the optimized porosity for enhanced dihydrogen binding and storage capacity that could meet DOE 2010 targets. By varying the separation and diameters, foams with different porosity are generated and their storage capacities are computed and compared as shown in Figure 1. The accessible surface areas have also been calculated using N_2 as the probe gas, which enables a direct comparison with Brunauer-Emmett-Teller specific surface area data. Among the similar mass density foams, the (5,5)+(10,0) is the optimum for storage (computed by the GCMC simulations) with the gravimetric (6 wt%) and volumetric (60 g/L) capacities at 77 K exceeding the DOE targets on a materials basis.

The effect of quantum corrections (QC) on the storage capacities has been estimated. The QC in C-H₂ and H₂-H₂ potentials essentially adds some repulsion

FIGURE 1. a) Optimized structure of the constant mass density 3D nano-foams. Corresponding accessible surface areas are also shown. b) The gravimetric and volumetric % of H₂ in the nano-foam obtained by GCMC. The left and right plots are obtained using weak [III] and strong [III] C-H₂ potentials.

and depends on temperature. The storage capacity computed without QC are overestimated by as much as ~5% (298 K) and ~20% (77 K). Including quantum corrections is important for accurate comparison of storage capacities with the DOE targets.

Spillover Catalysts

The effect of hydride formation on the catalytic activity of metal clusters has been evaluated. In order to assess this, we have separately calculated the chemical potential of H in the Pd-hydride crystal (PdH_{0.75}). The result is shown in Figure 2a (also shows the complete process of spillover) by the red line, which lies ~60 meV above the gray CH-line. Hence, in the case of Pd the spillover will occur before hydride formation. We also calculated the adsorption energies of the H on a Pd(111) surface, for coverage from 0.25 ML to 1 ML, shown by the red block in Figure 2a. The adsorption energy of 0.25 ML hydrogen is 0.57 eV, only slightly higher (~0.1 eV) than that in the Pd₄ cluster. Hence, with increasing cluster size the threshold of the spillover may decrease but not very significantly. The spillover analysis has been extended to Ni shown in Figure 2b. Overall the less expensive Ni behaves similarly to the Pd.

The weak binding of metal catalyst on graphene substrates leads to agglomeration, which reduces the wt% of spillover H₂. In order to maximize the storage wt% via spillover well-dispersed smaller sized catalysts are required. We show that doping of the graphene with B or N improves the binding energy of the catalyst significantly, which is desired to obtain well-dispersed catalysts on graphene. Furthermore, the effect of doping on the spillover has also been explored. Boron has very little effect on the spillover. However, in the case of N-doping, the binding energy of first H₂ is significantly reduced, and entropy-driven spillover can begin essentially from the very first adsorbed H₂, improving the net capacity. Therefore, both B and N are not only good anchors for individual transition metal (TM) atoms (as shown

FIGURE 2. a) Left: Schematic of spillover process in real space. The inequality shows the range of chemical potential μ_H favorable for spillover. Right: model of spillover in energy space displays the relative energies (chemical potential) of H in different states. The gray, dark-red, and blue lines show the μ_H in fully hydrogenated graphene (CH), in metal hydride, and in the H_2 molecule, respectively. The pink and dark-red blocks show the range of energies of H at the catalyst and at the Pd(111) surface with the H coverage varying from 0.25 to 1 ML. The family of thin dark-blue lines corresponds to the energies of H bound to graphene. b) The optimized structure of Ni_4H_{2n} ($n = 2$ to 10). The plot of incremental energy E_{incr} versus number of H atoms. The grey line shows the H binding energy in fully hydrogenated phase. The E_{incr} crosses this line after 6th H_2 molecule, indicating the thermodynamic onset of spillover.

previously at the National Renewable Energy Laboratory) but also for spillover catalysts.

Metallacarboranes

We continue our effort in designing materials incorporating TM atoms, which can bind dihydrogen via Kubas interaction while avoiding the clustering of TM atoms. We show that a high hydrogen storage capacity can be obtained in metallacarboranes via the TM atoms reversibly binding up to 5 dihydrogen, as shown in Figure 3. Sc and Ti were found to be optimal among the first row TM atoms maximizing the H_2 storage density to ~8 wt% on the metallacarborane. The calculated binding energies are within the range needed for reversible adsorption. Being an integral part of the cage, the TMs do not suffer from clustering problems, which have been an issue for the development of TM decorated graphitic materials. Furthermore, carbon atoms in the

FIGURE 3. Optimized structure of fully saturated metallacarboranes, wt% and binding energies eV/ H_2 are shown.

cage can bind other metallacarboranes to form metal organic frameworks.

Superacids

High surface area carbon samples supplied by Channing Ahn, Caltech, have been converted to a carbon nanotube salt and tested for hydrogen uptake. Initial studies suggest that converting a high surface carbon substrate to a superacid with charge separation stabilized via BF_3 complexation does not improve H_2 storage significantly as shown in Figure 4, and needs further testing.

Conclusions and Future Directions

- The pore sizes of 3D foams were optimized to maximize the storage capacity. The importance of quantum corrections to the interaction potentials was demonstrated.
- The effects of hydride formation and size of the catalyst on the catalytic activity of metal clusters were investigated and are found to be minimal.
- B and N dopants help to stabilize well dispersed spillover catalyst on carbon supports. The N doping leads to enhanced kinetics.

FIGURE 4. a) Adsorption isotherm of BF_3/F_2 -treated MSC-30 sample at 100°C, (wt gain 19%). Inset shows the isosteric heat as a function of surface excess adsorption. Limiting zero-coverage adsorption enthalpy is approximately 6.1 kJ/mol, consistent with that of pristine MSC-30. b) For comparison, the adsorption isotherm of pure MSC-30 (3350 m^2/g). Inset: isosteric heat. The zero-coverage enthalpy for MSC-30 was approximately 6.2 kJ/mole.

- Metallacarboranes were demonstrated to store ~8 wt% of hydrogen and can meet the DOE targets.
- Converting a high surface carbon substrate to a superacid with charge separation stabilized via BF_3 complexation did not demonstrate significant improvement in H_2 storage but needs further testing.
- Future spillover thermodynamics work: Study the effect of surface modification on the thermodynamics and kinetics of spillover. Evaluate the effect of curvature, size of metal cluster, anchors, and bridges on the migration barriers of H from the activator to the receptor. The possibility of transport of atomic H, as the recombination will not occur due to violation of the momentum conservation.
- Use foams as a model to quickly assess the storage capacities of porous carbon materials. Optimize

both gravimetric and volumetric contents with respect to accessible surface area. Complete development of the GCMC-evaluator and include the quantum corrections for more accurate realistic isotherm. Calibrate the predicted capacities with results from known materials.

- Search for lighter metal atoms (e.g. Ca) to maximize the wt% in metallacarboranes. Effect of linkers on the wt and volume%. Suggest optimized structures for metallacarboranes-based MOFs.
- Continue our work on dynamics of the chemically bound/absorbed hydrogen atoms: barriers and sigmatropic selection rules for H-hopping. Diffusion of H atom from catalyst to graphene and the rate of spread, quantitative front propagation model in contrast to conventional $\langle r^2 \rangle \sim D \times t$ diffusion.
- Conversion of nitrogen doped p-delocalized carbon systems such as giant fullerenes, VANTA, and activated carbon, to superacid salts and test for hydrogen storage. High-pressure Fourier transform infrared studies of curvature dependent hydrogen spillover. Continue the testing on VANTA.

Special Recognitions & Awards/Patents Issued

1. Our work published in Nano Letters was selected as a Cover article (March 2008).
2. DOE Hydrogen Program R & D Award (June 2008).
3. B.I.Y. received 2008 Nanotech Briefs Nano 50 Innovator Award (July 2008).

FY 2009 Publications

1. "Hydrogen storage by spillover on graphene as a phase nucleation process", Y. Lin, F. Ding, and B.I. Yakobson, *Phys. Rev. B*, v 78, 041402-R (2008).
2. "Fullerene nanocage capacity for hydrogen storage", O.V. Pupyshcheva, A.A. Farajian, and B.I. Yakobson, Nano Letters, v 8, 767 (2008) Cover article.
3. "H-spillover through the catalyst saturation: An ab initio thermodynamics study", A.K. Singh, M.A. Ribas, and B.I. Yakobson, ACS Nano, v 3, 1657 (2009).
4. "Comparative evaluation of carbon-foams hydrogen storage capacity through Monte-Carlo simulations", A.K. Singh, J. Lu, R. Aga, and B.I. Yakobson, in preparation.
5. "Metallacarboranes: A promising new hydrogen storage material", A.K. Singh, A. Sadzadeh, and B.I. Yakobson, in preparation.

FY 2009 Presentations

1. "Nanoclusters and surfaces for H storage", Boris I. Yakobson, DOE CMSM-08 coordination meeting in Gatlinburg, TN, Oct 30 – Nov 1, 2008.

2. Lecture on “Computations for Applied Nanostructures”, Lockheed-Martin Corp. Workshop, October 13–16, 2008.
3. “Exploring nanostructures with a computer: hydrogen confinement on carbon”, Department of Mechanical Engineering, University of Houston, Texas, February 26, 2009.
4. “Carbon nanostructures for molecular hydrogen confinement”, A.K. Singh, F. Ding, R.S. Aga, B.I. Yakobson, ACS Annual Meeting, Salt Lake City, April 26, 2009.

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IV.C.1e NREL Research as Part of the Hydrogen Sorption Center of Excellence

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Project Start Date: February 1, 2005

Project End Date: Project continuation and direction determined annually by DOE

hydrogen binding energy in the range of 15–20 kJ/mol (for room temperature operation).

- Decrease heat-transfer requirements to increase on-board refueling times.
- Sorption materials typically meet DOE refueling and delivery rate targets.
- Close the gap between the idealized sorption materials that have been predicted and the synthesis of actual materials using low-cost source materials and synthesis processes such that cost target will be achieved.
- Cost: Typical high-surface-area, lightweight materials (e.g., activated carbon) are commercially manufactured in bulk at ~\$1/kg with carbon costs being only a small fraction. Thus, material costs for a system could be ~\$15/kg-H₂ (assume 7 wt%).
 - Develop sorbents using inexpensive materials and processes.
- Impact: NREL's H₂ storage material goals provide DOE with viable solutions that have the potential to meet even the ultimate technical targets. While this requires revolutionary materials, breakthrough technologies are being pursued.

Objectives

NREL's research in the Hydrogen Sorption Center of Excellence (HSCoE) is targeted at addressing key technical barriers in DOE's Program for On-Board Hydrogen Storage:

- Weight and Volume: System capacities approach material capacities as the tank operation moves toward ambient temperatures and pressures with materials that have optimum binding energies. In general, sorbents already meet the vast majority of DOE hydrogen storage targets and have minimal heat transport requirements. NREL development efforts focus on the remaining targets, e.g., cost and capacity.
 - Volumetric and gravimetric capacities are closely linked in sorbents.
 - Increase material density (i.e., >0.7 g/ml) to decrease size.
 - Increase specific surface area and optimize pore sizes to decrease tank weight/size.
 - Optimize binding energies to increase capacities and operating temperature.
 - Develop the highest-efficiency storage system by optimizing sorbent materials that operate reversibly on-board with a

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage technical barriers section of the Fuel Cells Technologies Multi-Year Research, Development and Demonstration Plan:

General:

- (A) System Weight and Volume
- (B) System Cost
- (C) Efficiency
- (D) Durability/Operability
- (E) Charging/Discharging Rates
- (J) Thermal Management

Reversible On-Board:

- (P) Lack of Understanding of Hydrogen Physisorption and Chemisorption
- (Q) Reproducibility of Performance

Technical Targets

This project is developing sorption materials for hydrogen storage systems. In general, the effort

focuses on creating hydrogen adsorption materials with optimized binding energy (10–25 kJ/mol) such that the system may operate at near-ambient temperatures and moderate pressures (Table 1). The design and synthesis of these hydrogen storage materials is aimed at meeting the following DOE hydrogen storage targets:

- Cost: \$4/kWh net
- Specific energy: 1.8 kWh/kg
- Energy density: 1.3 kWh/L
- Charging/Discharging Rate: 3.3 min

Accomplishments

- Developed novel scalable synthetic processes (e.g., templating) to form high-surface-area, lightweight materials with optimum pore structure and composition for H₂ storage. These techniques accelerate development by increasing appropriate material synthesis rates where all the higher H₂ binding energy sites are accessible.
- Developed materials with ~15% B substitution in C and demonstrated that this increases capacity and binding energy. The enhanced binding energy is sufficient to store substantial hydrogen within the

DOE target temperature range of ~220 to 350 K; in good agreement with theoretical models.

- Theory and experiment continued to iteratively interact to design and synthesize several new H₂ storage materials. From the outset of the HSCoE, the ability to synthesize, stability, and DOE targets have been selection criteria for the design of new materials. Also, theory always works closely with experiment to find viable synthetic paths.
- Validated the initial theoretical prediction of single metal atoms dispersed and stably supported on a matrix being able to reversibly hold more than 2 H₂ [1]. This was done by demonstrating that the same models accurately predict the number of H₂ molecules adsorbed and the binding for the Ti-Silica system [2]. This removes all doubt to the validity of the predictions and indicates that we have routes to meeting DOE's ultimate storage targets.
- Identified new inexpensive materials that use the unique properties of Ca with very viable synthetic routes. These revolutionary new materials could store H₂ at >100 g/L and >10 wt%, exceeding all of DOE's ultimate targets including cost and volumetric/gravimetric capacities [3].

TABLE 1. Summary of Hydrogen Storage Properties for Materials Developed by NREL in Fiscal Year 2009

Storage Parameters/ Materials	Specific Energy (Net, wt%)	Volumetric Energy (Net, g/L)	Binding Energy (KJ/mol)	Conditions	Besides Cost, other targets of issue	Comments
DOE Targets	5.5	40	NA			
BC _x (E)	1.4	1	11	77 K, 2 bar		Only 240 m ² /g, 3x more than AC with same SSA
2.7 H ₂ -Ti-Amor-silica (T)	NA	NA	31	2.4 H ₂ /Ti		Agrees w/2.7 H ₂ /Ti exper.
Li-BC ₈ (E)	NA	NA	10-15	RT, 1 bar		10x gain over AC, 5 m ² /g
CaC ₁₄ (H ₂) ₈ (T)	>10	>100	20-40	RT		Proof of unique Ca properties
Ca-COF(H ₂) ₄ (T)	5.6	44		RT		Viable synthesis material
Hopping spillover kinetics (T)	NA	NA	~30	RT		1 st viable kinetic mechanisms
Hole assisted Kinetics (T)	NA	NA	~50	RT		1 st viable kinetic mechanisms
Ru, Pt, Pd-AC spillover (E)	1.2	6	20	RT, 80 bar	Catalyst, rate	Spillover on AC reproduced, 5x increase low P, higher rate
Li/THF co-int. Graphite (T)	5-7		5-20			
Li/THF co-int. Graphite (E)	0.5	NA		77 K 2 bar		Need to remove excess tetrahydrofuran
Li/THF co-int. Aerogel (E)	2.4	NA		77 K 2 bar		Down selected, not working
Ni(BF ₄) ₂ (PPh ₂) ₂ - SiO ₂ aerogel (E)	~1	NA	20	77 K, 2 bar		Model system that showed coordinated Ni-H ₂ binding. Down Selected, low capacity
Sc,Fe,Cr-organometalics (T)	4-8	20-40	15-25	ambient		
Sc,Fe,Cr organometalics (E)	NA	NA	NA	ambient		Down selected, little progress

NA – not applicable; E - experiment; T - theory; AC – activated carbon; SSA – specific surface area; RT – room temperature ; w/ - with

- NREL identified that barriers to migration are lowered sufficiently to enable spillover via structural and electronic features, and/or quantum mechanical tunneling where H will diffuse before it desorbs. These results provide development paths to create higher-capacity, higher-rate H storage spillover materials that can be used to meet DOE targets.
- NREL developed new catalyst processing that improved spillover capacity and charging rates. The decreased processing time, scalability, and improved performance will accelerate spillover materials' development to meet DOE targets.
- NREL identified potential issues that produce irreversibilities and cause irreproducible hydrogen sorption measurements. An improved understanding of surface functionalization will enhance spillover.
- NREL improved measurement capabilities to provide more accurate and unique hydrogen storage materials characterization at high throughput.

Introduction

NREL is leading the HSCoE to develop reversible sorbent materials for hydrogen storage within the U.S. DOE National Fuel Cell Technologies Program focused on vehicular and early market applications. The HSCoE is developing the science base and technology advances required to meet DOE storage goals by investigating a range of hydrogen sorbent materials. NREL performs research and development within the HSCoE on a variety of nanostructured and high-surface-area materials that may include carbon, metals, oxygen, and other lightweight elements. These materials show promise for breakthrough performance in hydrogen storage.

A guiding principle in developing the required material is that a continuum of energies exists for hydrogen bound to substrates and molecules. On the weak side of the continuum is non-dissociative physisorption due purely to van der Waals forces (4 kJ/mol). On the strong side is the full C-H chemical bond in methane with an energy of ~400 kJ/mol. Between these two limits, with binding energies between 10 and 50 kJ/mol, are the materials we are developing. The DOE goals can be met with sorption materials if (i) the energy for hydrogen adsorption can be designed to be in this optimal range, and (ii) efficient volumetric arrangement of a sufficient number of suitable binding sites can be achieved with a low-weight material. These goals are difficult to reach in conventional high-surface-area adsorbents that are limited by low physisorption binding energies, heterogeneity of the adsorbent surfaces and adsorption sites, and excessive macroporosity and poor volumetric packing.

Approach

To accelerate sorption materials' development, NREL is focused on four main areas:

- **Increase Matrix Binding Energy:** Increase concentration of substitution atoms (e.g., B for C) in lattices to adsorb dihydrogen directly (via donation), stabilize active species (e.g., transition metals) against agglomeration, and/or provide anchor points for building more complex sorbents.
 - 11 kJ/mol H_2 binding energy from B-substitution provides near-room-temperature sorption.
- **Increase Storage Site Access:** Develop stable high-surface-area, sub-microporous (<1 nm), light matrix materials that can either stabilize large quantities of hydrogen directly or provide frameworks for incorporating/stabilizing other components for hydrogen storage.
 - >2,500 m^2/g SSA with 0.7 to 1.2 nm pore sizes may provide >6 wt% cryocompression.
- **Form Multiple H_2 Binding Sites:** To exceed DOE 2015 and meet DOE ultimate storage targets, fundamentally new approaches must be developed to store >7.5 wt% and >70 g/L hydrogen.
 - Requires >1 H_2 adsorbed at each binding site and material densities >1g/ml.
 - NREL is pioneering development of materials with multiple dihydrogen molecules per binding site.
 - Use inexpensive chemical and gas phase syntheses of organometallics.
 - Use viability in designs; theorists outpaced experiment.
 - Identify >10 wt% and >100 g/L dihydrogen storage materials.
- **Develop Near-Ambient Temperature Hydrogenation:** Develop detailed understanding using lightweight materials to reversibly store hydrogen via weak chemisorption processes. Investigate surface functionalization and catalyst integration to improve storage thermodynamics and kinetics.
 - NREL observed C-H bonds on reversible charge/discharge hydrogenation.
 - Improve processes and measurements to make stable reproducible materials.

By promoting accelerated progress in each of these areas and then deploying the knowledge obtained for the fabrication of optimized materials, systems that meet the DOE storage targets will be developed. NREL development efforts leverage each other and balance H_2 and material reactivity with the density and stability

of the sorption sites. NREL's vast amount of material design, selection, synthesis, and testing is only partially summarized in this report.

Results

Increasing Access to Higher-Binding Energy Sites:

In general, materials with high specific surface area can be created via pyrolysis processing of non-porous materials. However, materials made this way tend to have heterogeneous surface structures and a broad range of pore sizes, many of which are too large and thus have a substantial fraction of the hydrogen residing in the gas state rather than adsorbed onto surfaces. Creating optimized geometric structures in which all of the sorption sites are accessible to hydrogen requires the careful design of materials and the processes used. This issue is the same regardless of the sorption mechanism being employed, but does require that the structures be optimized for the desired type and conditions of the hydrogen storage. Templating is one technique being employed by NREL to enable systematic investigations of how specific structures and compositions affect hydrogen storage properties. Templating involves the vapor or chemical-phase deposition of a partial or full layer of material onto a porous structure. If, for example, carbon is coated onto a zeolite/template, the zeolite/template can be removed via chemical or vapor processing, leaving behind a porous carbon material that matches the geometric structure of the removed zeolite/template. This type of process has been used to make highly porous carbon materials (i.e., with specific surface areas over 3,500 m²/g) with pores that are nearly identical to the zeolite; resulting in materials with ~7 wt% hydrogen storage capacities [4]. NREL has used this technique to make novel lightweight hydrogen storage materials with optimized compositions and pore structures mimicking the template chosen. This technique accelerates development by increasing the synthesis rate of appropriate materials in which all the higher hydrogen binding sites are accessible.

Increasing Hydrogen Binding Energy with

Substituted Elements: NREL uses templating to make high-SSA materials, but more importantly, we have used this technique to make materials with higher binding energy sites. These higher binding sites are due to optimized pore sizes in the range of 0.4 to 1.2 nm, and/or they are associated with boron substitution in a carbon lattice (experimental demonstration of ~11 kJ/mol agrees well with calculations). Interest in the use of boron-substituted carbon nanomaterials has increased due to observed increases in hydrogen storage capacity through both computational and early experimental studies. This enhanced adsorption capacity will occur at all temperatures and thus enables improved near-ambient-temperature (i.e., ~220 to 350 K) hydrogen storage. Apart from using these

substituted nanostructures on their own, the boron (and possibly nitrogen-substituted carbon) sites also provide a means for partially coordinating and stabilizing metal atoms to create complexes that more strongly bind dihydrogen or enable multiple dihydrogens to be adsorbed at each metal site [5].

The main challenges for creating highly loaded boron substituted carbon include:

- As the boron composition increases, the specific surface area tends to decrease.
- The boron must be sp² coordinated in the carbon structure to enhance binding properties.

NREL is developing processes to form B-substituted C materials with high B composition and high SSA. For example, the use of vapor phase boron trichloride with benzene at ~1,100 K is a well-known process that forms BC_x films [6]. NREL uses this and other processes to deposit BC_x films on templates. By controlling the processing conditions and precursor materials, NREL produced materials with ~15% boron substituted in the carbon lattice. With X-ray photoelectron spectroscopy (XPS) data, we can quantitatively determine the amount of B and the binding environment (Figure 1). These XPS data indicate that the B in the BC_x materials is typically in multiple binding states. However, by changing the processing conditions, we can increase the amount of B in the appropriate binding state that enhances adsorption. Through the use of temperature-programmed desorption (TPD) measurements, NREL also demonstrated that BC_x materials store hydrogen more strongly than, for example, the template material being used, and that changes in processing affect the amount of B in the materials and the amount of hydrogen stored (Figure 2). As seen in Figure 2, as

FIGURE 1. XPS of BC_x materials – the multiple B peaks indicate that the boron has multiple coordination states.

the boron composition in the BC_x films increases, the hydrogen measured by TPD increases and is typically ~100 times more than what is observed with the template materials alone, under the same conditions. NREL will continue improving the BC_x processing to create hydrogen storage materials with B compositions over 20% and specific surface areas over $3,000 \text{ m}^2/\text{g}$, and should demonstrate net hydrogen storage material capacities $>5 \text{ wt}\%$, $>50 \text{ g/L}$ at $\sim 220 \text{ K}$. NREL will use XPS, infrared spectroscopy, nuclear magnetic resonance, and neutron scattering to quantify the electronic and hydrogen storage properties of the BC_x materials to help guide and accelerate the improvement of the materials.

Coordinated Metal Centers to Enhance Hydrogen Sorption: NREL has championed the use of lightweight metals (i.e., first-row transition metals and group I and II elements) to enhance the binding of dihydrogen on matrix materials and, perhaps more importantly, the ability to create sorption sites that can store more than one dihydrogen molecule [1]. Since the publication of our seminal paper in this area, theorists and experimentalists have worked closely at NREL to iteratively design and synthesize new materials with coordinated metal centers. From the outset, we have strictly adhered to the criteria of synthesizing stable materials that have the potential to meet DOE hydrogen storage targets. Thus, theorists not only identify new materials, but work with experimentalists to identify thermodynamically viable synthetic paths to form stable materials. In addition, the calculations used to identify these novel materials have been validated with all known 3d metal- H_2 experimental results. Thus, there is good agreement for both the binding energy and the number of dihydrogens being stored between the theory and the known experimental results.

FIGURE 2. TPD (inset) measurements of templated BC_x materials made by NREL indicate that the hydrogen storage capacity at $\sim 200 \text{ K}$ and vacuum pressure increases with increasing boron concentration. Since these results were performed under vacuum pressures, the data indicate that the hydrogen is more strongly bound by the BC_x materials than is typically observed with porous carbon materials.

While single metal atom decoration of pure element matrices is possible without metal agglomeration, metal atoms are typically stabilized further at dopant sites (e.g., boron in carbon), and/or with H ligands. Thus, while several investigators have attempted to synthesize materials with single metal atoms coordinated on surfaces, most materials synthesized to date may only be marginally stable, and thus positive results have to date been limited. In addition, the reactivity of coordinated but electronically active metal sites indicates that great care must be taken to ensure that contamination and durability issues are adequately addressed. Recently, metal organic framework (MOF) materials with open Mn metal sites were fabricated with strong dihydrogen binding [7]. These results were in very good agreement with NREL's calculations [5] (experiment $1 H_2$ at 10 kJ/mol ; theory $1 H_2$ at 8.4 kJ/mol), making this another example that confirms our models. However, the recent work by Hamaed et al. [2] is perhaps the most compelling confirmation to date. In this work, Ti dispersed on amorphous-silica internal surfaces are coordinated via strong Ti-silanol bonds (i.e., $\sim 400 \text{ kJ/mol}$). However, each Ti atom still has sufficient reactivity to adsorb multiple dihydrogen molecules. Once again, the experimental results ($2.7 H_2$ at $<22 \text{ kJ/mol}$) and models ($2.4 H_2$ at $<31 \text{ kJ/mol}$) are in good agreement. But more importantly, these experimental results confirm the basic premise of NREL's original work that an open metal site can store more than 2 dihydrogen molecules with energies appropriate for reversible hydrogen storage at ambient temperatures.

NREL worked with Lawrence Livermore National Laboratory (LLNL) over the previous year to form similar open Ni metal centers via $Ni(BF_4)_2(PPh_3)_2$ - SiO_2 aerogels. In this work, we experimentally measured $1 H_2/Ni$ at $\sim 25 \text{ kJ/mol}$, which again was in good agreement with theoretical estimates. (More information about the process is available in the LLNL section of this report, see IV.C.1j.) In this work, NREL and LLNL experimentalists and modelers worked closely to identify and systematically develop materials using well-established chemistries. Based on the successes of the Ni-silica aerogel and Ti-silanol work, we have fully validated the designed-material approach to forming strong dihydrogen adsorption with open metal centers. This work is applicable to most metals (e.g., Li, Na, Mg, Ca, Sc, Ti, V, Mn, Co) and matrix materials. However, NREL will apply our expertise to designing and synthesizing more stable and promising materials. For example, NREL has experimentally demonstrated that B substituted in carbon stabilizes open metal atoms to enable stronger dihydrogen binding. NREL demonstrated these principles with Li, Co, and Fe; all of these indicate that, in agreement with theory [1], the metal-matrix binding and the specific metal atom affect the number and binding energy of dihydrogen.

In the case of Li and possibly most solution-phase processes, boron substitution in carbon is required to stabilize the Li atoms and enable dihydrogen adsorption. With our unique promising results, NREL will pursue materials/process optimization to increase the number of viable binding sites and ultimately the overall storage capacities.

In this regard, NREL was the first to submit a paper that identified the special properties of inexpensive Ca. Here again, NREL applied our unique predictive M-xH₂ theories to investigate the hydrogen storage properties of group I and II metals. Unlike Li, Na, and Mg, Ca can be coordinated to matrix materials in such a way that a pseudo 3d band state forms, enabling substantial amounts of dihydrogen to be reversibly adsorbed. For example, Ca-intercalated graphene (Figure 3) with the graphene layers separated sufficiently to allow dihydrogen molecules access around the Ca atoms, has the potential to have net hydrogen capacities in excess of 100 g/L and 10 wt%. In this case, the Ca atoms are stabilized by the carbon with a +1.3 charge transfer at 50–90 kJ/mol. Furthermore, the Ca atoms adsorb dihydrogen at 20–40 kJ/mol. The Ca-C binding and charge transfer are sufficiently strong to prevent Ca clustering; they become weaker as more dihydrogens adsorb. The Ca-xH₂ binding is sufficient to store and release dihydrogen at densities much higher than liquid hydrogen, but at ambient temperatures and moderately low pressures (i.e., 4 to 30 bar). Even though the synthetic pathways remain a challenge, this set of work provides a breakthrough that clearly defines sorbent materials that could be used to meet DOE's ultimate storage targets.

In addition to the initial Ca-graphene work, NREL also found that graphitic B-C and some covalent-organic framework (COF) and MOF materials stabilize open Ca centers. In the case of COFs (Figure 4), two Ca atoms

FIGURE 3. Novel calcium-intercalated graphene materials have exceptional hydrogen storage capacities over 100 g/L and 10 wt%. In this case, the Ca atoms are stabilized by the graphene at a +1.3 charge, which is sufficient to prevent agglomeration.

will be bound to the benzene linkers at ~120 kJ/mol, which in turn will adsorb four dihydrogen molecules with an average binding energy of 15 kJ/mol. Although this particular material will have a hydrogen storage capacity of only ~44 g/L and 5.6 wt%, the theorists and experimentalists have worked together to identify materials with very viable synthetic pathways.

Weak Chemisorption of Hydrogen: The HSCoE is developing spillover materials to provide ambient-temperature hydrogen storage. NREL's efforts to develop weak-chemisorption hydrogen storage materials include:

- **Improved spillover material processing** to reproducibly make materials with higher kinetics and hydrogen storage capacities. In general, improved catalyst processing increases hydrogen storage rates and capacities. Thus, NREL developed processes that drastically reduced the deposition times and uniformly deposited catalyst with particle sizes to >1 nm with several different metals (e.g., Pt, Pd, Ru) on different types of receptor materials (e.g., activated carbon, BC_x). Initial results indicate that NREL's improved catalysts were stable for multiple cycles, and the low-pressure hydrogen uptake increased by a factor of five (Figure 5). The BC_x material also improved spillover material properties. In addition, the spillover binding energies for these materials were measured to be ~20 kJ/mol, and the higher-pressure loading improved to ~85% of maximum in ~5 minutes, which is a substantial

FIGURE 4. COF materials will stabilize two Ca atoms at each benzene linker to form a hydrogen storage material in which each Ca atom can reversibly adsorb 4 dihydrogen molecules to provide ~44 g/L and 5.6 wt% storage at ~15 kJ/mol. The Ca is bound to the COF benzene linker at ~120 kJ/mol, which does not collapse when the Ca is added.

FIGURE 5. Hydrogen spillover results indicate that improved catalyst processing enhances capacity (top). Irreproducibility in the processing often results in limited hydrogen spillover. However, with appropriate processing, hydrogen spillover (e.g., Ru on CMTEC data) is observed (bottom).

improvement from <60% for previous spillover materials. In general, NREL's catalyst deposition processing is scalable to large quantities, is applicable to inexpensive catalyst material (e.g., Ni), and may enable the use of substantially less catalyst. The decreased processing time, scalability, and improved performance will accelerate spillover materials' development while reducing costs to meet DOE targets.

- Surface Functionalization:** NREL identified potential issues that produce irreversibilities and cause irreproducible hydrogen sorption measurements. In general, surface composition and properties of the receptor material are important for hydrogen diffusion. For example, reactions with oxygen surface moieties can inhibit or promote hydrogen spillover. TPD analysis of desorbed gases from spillover samples indicates that when some oxygen moieties are present, reduction processes occur to form water, CO₂, CO, CH₄, and other hydrocarbons. This indicates that

some functional groups interact with the absorbed hydrogen to create irreversible chemical reactions. This result explains some of the irreversibility and hysteresis observed in some data, and indicates the importance of monitoring the effluent from spillover measurements to ensure that the hydrogen storage capacity results are being accurately determined. From our work, because higher oxygen content in the receptor material resulted in higher secondary-reaction products such as water, we recommend that careful analysis be performed whenever oxygen is present in the spillover materials. NREL will continue to systematically perform research with model systems in conjunction with calculations and species-specific characterization, (e.g., TPD, Fourier transform infrared spectroscopy, Raman scattering, neutron scattering, and nuclear magnetic resonance [NMR]) to further define how surface species affect H spillover processes including enhancing diffusion and capacities.

- Discovery of H Diffusion Mechanisms:** NREL was the first to identify that barriers to migration are lowered sufficiently to enable spillover via structural and electronic features, and/or quantum mechanical tunneling where H will diffuse before it desorbs. While previous work at NREL and in the HSCoE established the thermodynamic principles for hydrogen dissociation and transport from the catalysts, and for atomic hydrogen storage on the receptor materials, the specific mechanisms for hydrogen diffusion on the receptor materials are not clearly understood. Based on calculations, NREL identified that H migration increases substantially via hopping between surfaces that are closely spaced (Figure 6). This suggests that perhaps layered or corner structures may enable hydrogen atom diffusion via hopping. Similarly, calculations indicated that free holes lower the barrier energy of H atom diffusion due to the H strong negative-potential behavior. In this case, the barrier drops for graphene from 1.04 eV H⁰ to 0.60 eV for H⁺ and for MOFs from 1.52 eV H⁰ to 0.52 eV for H⁺. Thus, doping, defects, or functionalizations that form holes may enhance hydrogen storage via spillover. Finally, ambient-temperature quantum tunneling lowers the diffusion barrier energy. These results provide development paths to creating higher-capacity, higher-rate H-storage spillover materials that may be used to meet DOE system targets.

NREL Collaborations and Partnerships: As HSCoE lead and a leader in H₂ storage materials development and measurements, NREL collaborates with a large number of groups and institutions around the world. This includes working with the HSCoE partners, DOE Basic Energy Sciences projects, and independent projects, and participating directly with the HSECoE and the DOE Storage System Working

FIGURE 6. Initial calculations at NREL identified that, compared to migration along a surface, hopping between closely spaced surfaces substantially lowers the barrier for hydrogen diffusion.

Analysis Group. These interactions have led to several joint publications, and NREL has performed ~200 sample measurements this year to assist partners and collaborators in characterizing their hydrogen storage materials.

Conclusions

- Experiments validate the original NREL predictions that single metal atoms dispersed and stably supported on a matrix can reversibly hold more than 2 H₂. NREL was the first to use this theory to identify the unique properties of Ca.
- Experiment and theory worked together to identify new inexpensive Ca-based materials with viable synthetic routes to store H₂ at >100 g/L and >10 wt% at ambient temperatures. Since these materials will exceed liquid hydrogen densities at ambient temperatures, they may be used to meet DOE's ultimate targets including cost and capacities.
- Systematic experiments determined that improved surface/material processing increases spillover capacity and sorption rates. Some surface modifications including substitution, functional groups, and post-treatments affect the hydrogen storage capacities for spillover.
- Oxygen and other functional groups can react with spilled-over hydrogen to form irreversible and irreproducible chemical reactions that may adversely affect the reversible hydrogen storage capacity. Additional measurements need to be routinely performed to ensure that secondary reactions are not accounting for substantial amounts of the measured hydrogen storage capacities.

- NREL was the first to identify potential mechanisms that lower the barrier to hydrogen diffusion on receptor materials. Hopping between closely spaced surfaces, free-holes, and quantum-tunneling effects can all substantially increase hydrogen migration. These insights provide pathways for improving hydrogen spillover capacities and kinetics.
- NREL developed templating techniques to create high-specific-surface-area carbon and BC_x materials.
- NREL developed B-substituted carbon materials with ~15% boron and relatively high specific surface areas. The B needs to be in sp² coordination to enhance dihydrogen binding. Thus, NREL needs to increase the B concentration, the amount of B in the correct state, and the specific surface areas of the materials.
- Open metal center coordination is stabilized at boron and nitrogen sites substituted in carbons. In addition, these materials enhance spillover capacities when a catalyst is deposited.

Future Directions

FY 2009

- Optimize templating processes to synthesize high-surface-area materials with >2,500 m²/g, <1 nm pore diameters, and/or boron concentrations >20%.
- Develop/improve gas-phase synthesis of targeted carbon and non-carbon sorbents.
- Create stable, coordinated, unsaturated metal centers with higher site densities that have substantial hydrogen storage using inexpensive materials including Li, Na, Ca, transition metals, and BC_x.
- Use model systems and processing to construct specific surface features to test designs for improving spillover.
- Perform appropriate characterization (infrared, Raman, TPD, Neutron scattering, NMR) to determine the H state on the receptor.
- Accelerate theoretical efforts to design viable materials and synthetic routes.
- Continue to develop state-of-the-art measurement techniques and to provide high-throughput measurement for partners.
- Down-select materials and help with center go/no-go decisions based on material/system potentials.

FY 2010

- Wrap up materials development and characterization and work with the hydrogen sorption community to recommend materials/routes for future development efforts.

- Scale up synthesis of most promising materials for round-robin verification of samples.
- Provide materials/systems recommendations for HSECoE.
- Determine viability of high-surface-area materials to meet DOE 2010, 2015, and ultimate targets.
- Quantify the enhancements produced by substitutions for dihydrogen binding and metal stabilization.
- Demonstrate the ability to form and quantify the H₂ binding of metal centers and their ultimate storage potential.
- Quantify the potential of weak chemisorption along with the effects of intrinsic and functionalized material properties.

Special Recognitions and Awards/Patents Issued

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8. “Mechanism of Hydrogen Storage on Reduced Carbon Single-Walled Nanotubes,” Calvin J. Curtis, Thomas Gennett, Chaiwat Engtrakul, Kevin O'Neill, Jamie E. Ellis, and Michael J. Heben, *Fall MRS Proceedings* (2008).
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- 1.** DOE HSCoE Overview, A.C. Dillon (invited talk) DOE Annual Merit Review, May 18-21, 2009.
- 2.** Hydrogen Sorbent Development within the HSCoE, L.J. Simpson (invited talk), DOE Annual Merit Review, May 18-21, 2009.
- 3.** Novel H₂ storage approaches using organometallics, Shengbai Zhang, (invited talk) APS March Meeting, Pitt., PA, Mar. 19, 2009.
- 4.** First-principles study of dihydrogen interaction of porphyrin-like nitrogen-doped graphenes, Woon Ih Choi, Seung-Hoon Jhi, Kwiseon Kim, and Yong-Hyun Kim, APS March Meeting, Mar. 19, 2009.
- 5.** Nanostructured Adsorbents for Hydrogen Storage, L.J. Simpson, K. O'Neill, P.A. Parilla, C. Engtrakul, T.G. Gennett, J.L. Blackburn, Y. Zhao, A.C. Dillon, E. Whitney, C. Curtis, and M.J. Heben, APS March Meeting, Pittsburgh, PA, Mar. 19, 2009.
- 6.** Energy storage in nanostructured materials, Y-H Kim, (invited talk) APS March meeting, Mar. 16, 2009.
- 7.** Overview of the DOE Hydrogen Sorption Center of Excellence, A.C. Dillon, (invited talk) DOE Tech Team Review, Detroit, MI, Jan. 15, 2009.
- 8.** Theory Activities in HSCoE, Y. Zhao, (invited talk) DOE Tech Team Review, Detroit, MI, Jan. 15, 2009.
- 9.** Cluster 4: Spillover (Weak Chemisorption), T.G. Gennett, (invited talk) DOE Tech Team Review, Detroit, MI, Jan. 15, 2009.
- 10.** Strong Binding of H₂ (RC3) Technical Update, Chaiwat Engtrakul, (invited talk) DOE Tech Team Review, Detroit, MI, Jan. 15, 2009.
- 11.** Mechanism of Hydrogen Storage on Reduced Carbon Single-Walled Nanotubes, Calvin J. Curtis, Thomas Gennett, Chaiwat Engtrakul, Kevin O'Neill, Jamie E. Ellis. and Michael J. Heben, Fall MRS proceedings 2008.

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IV.C.1f Hydrogen Storage Media through Nanostructured Polymeric Materials

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Project Start Date: July 1, 2007
Project End Date: June 30, 2012

It supports DOE's initiative in developing adsorption-based storage technology with high uptake capacity, reversibility, and stability. The successful outcome of the project will produce a new storage material that meets the recently revised DOE 2015 targets:

- Gravimetric density: 1.8 kWh/kg
- Volumetric density: 1.3 kWh/L
- Cost: \$2/kWh net

Accomplishments

- Three classes of polymers with over 50 different structures were synthesized and characterized. Polymers with specific surface area (SSA) as high as $\sim 1,900 \text{ m}^2/\text{g}$ and tunable pore size from 0.6 to 0.9 nm were prepared.
- Excess H_2 uptake of 5.1 wt% at 77 K (40 bar) was achieved, a nearly 150% improvement over Fiscal Year 2008 results.
- H_2 -polymer interactions were investigated through a) theoretical and experimental studies on the heat of adsorption; and b) high pressure ^1H nuclear magnetic resonance (NMR) measurement on the state of hydrogen in the micropores.

Introduction

The capacity of on-board hydrogen storage is critical to hydrogen-powered fuel cell vehicles. For practical applications, the storage system must meet the gravimetric and volumetric densities as well as the cost target set by DOE. These requirements pose significant challenges to storage material development. We plan to address these challenges by exploring a new class of hydrogen adsorbent, nanostructured polymeric materials. Compared with other adsorbents, polymers have excellent thermal stability and tolerance to gas contaminants such as moisture. Polymers also have low skeleton density and high intrinsic porosity via covalent bonds, capable of maintaining SSA during high pressure pelletizing for better volumetric density. Furthermore, they can be produced at a commercial scale with the existing industrial infrastructure. Significant progress has been made in polymer gas adsorbent research [1-2]. Our approach focuses on improving hydrogen uptake capacity and the heat of adsorption by enhancing SSA, porosity, and framework-adsorbate interaction through rational design and synthesis at the molecular level.

Objectives

- To design, synthesize, and evaluate nanostructured polymeric materials (NPM) as new hydrogen storage adsorbents for transportation applications.
- To support materials development with in-depth understanding of hydrogen-NPM interaction through modeling/simulation and advanced characterization.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) System Weight and Volume
- (B) System Cost
- (C) Efficiency
- (D) Durability/Operability

Technical Targets

The focus of this project is to prepare NPMs as new hydrogen adsorbents with improved storage capacity and heat of adsorption through rational design, guided by computational modeling and advanced characterization.

Approach

Our design principles aim at improving the following attributes of the polymers: (a) high SSA to provide sufficient interface with H_2 ; (b) narrow pore diameter to enhance van der Waals interactions in the confined space; and (c) “metallic” features, either through π -conjugation or metal doping, to promote electronic orbital interactions with hydrogen. During FY 2009, we carried out parallel studies of three different categories of polymers. We continued our investigation on SSA enhancement and porosity regulation using simple aromatic monomers with contorted cores and hyper-crosslinking chemistry. We explored several nanoporous polymers with monomers containing heterocyclic functional groups for better conductivity or polarizability. We initiated study of the transition metals containing porous polymers either through post-doping or direct synthesis. The surface property, hydrogen uptake capacity, and isosteric heat of adsorption were measured through N_2 -Brunauer-Emmett-Teller (BET) and Sievert isotherm methods. In addition, theoretical modeling using ab initio and density functional theory (DFT) calculations were conducted to compare with the experimental results for better understanding of the hydrogen-polymer interaction. Through collaboration with our Hydrogen Sorption Center of Excellence (HSCoE) partners Professors Y. Wu and A. Kleinhammes of The University of North Carolina, the hydrogen-polymer interactions were investigated using high pressure 1H -NMR.

Results

We continued to explore new polymers with a variety of monomers and synthesis techniques as our main focus in FY 2009. We successfully prepared over 50 polymers using different monomers and synthesis schemes, followed by spectroscopic and surface characterizations. Shown in Figure 1 are 3-dimensional (3-D) drawings of several representative polymers. The hydrogen storage capacities were measured at both liquid nitrogen and ambient temperatures using a Sievert-type isotherm apparatus. The results for selected polymers are listed in Table 1. While SSA's of these polymers vary from ~ 900 m^2/g to nearly $1,900$ m^2/g , one common feature among them is the narrow pore size distribution, with most of the surface area from micropores with diameters between 6 to 9 Å. This is clearly demonstrated by Figure 2 in which the incremental surface area of a representative polymer is plotted as a function of pore size, calculated using a non-localized DFT method with the data obtained from N_2 -BET measurement. The most significant peak centers at 8 Å. This property represents a major difference from some other high SSA amorphous materials where the mesopores and macropores make up a significant fraction of the total surface area. The micropores in

FIGURE 1. 3-D Structures of Selected Polymers Prepared by Argonne and University of Chicago Team

TABLE 1. Hydrogen Adsorption Capacities for Selected Polymers

Sample	Gr. Uptake (77 K, 40 bar) ^a	Gr. Uptake (RT, 70 bar)	BET SSA (m^2/g)	Polymer type ^b
ANL-C1	4.0%	0.21%	1,233	C
ANL-C2	4.4%	0.35%	1,593	C
ANL-C5	5.1%	0.52%	1,863	C
UC-C10	2.8%	0.18%	1,043	C
UC-X4	3.2%	0.45%	971	X
UC-M12	3.6%	0.40%	1,060	M

^a Gravimetric uptake unit is (kg H_2 /kg adsorbent + H_{2ads})

^b C = polymers contains only aromatics, X = polymers with non-C element substitutions, M = polymers incorporated with transition metals
RT - room temperature

our polymers are generated by crosslinking of contorted monomers with the intrinsic hindrance at the molecular dimension, which is believed more efficient for hydrogen adsorption. At the macro-dimension level, the van der Waals interaction between different polymer strands or planes will minimize the voids through close packing. Figure 3 shows a DFT calculation of the 3-D structure of the micropore formed through the cross-linking of spirobifluorene. The pore size in the resulting structure is very similar to that measured experimentally. The computation model also individually places H_2 molecules inside of the pore with their position fully optimized, followed by the calculation of the binding energy for comparison with the experiment.

Isosteric heat of adsorption, ΔH_{ads} , is an important property for hydrogen adsorbents. To maintain sufficient anchoring of H_2 at ambient temperature without consuming excessive energy for extraction, the preferred ΔH_{ads} is from 15 kJ/mol to 20 kJ/mol. We investigated the heat of adsorption of several representative polymers designed for altering ΔH_{ads} by functional group, porosity, H_2 uptake level, etc. Shown in Figure 4 is the heat of

FIGURE 2. An Example of Incremental Surface Area as the Function of Pore Size for a Representative Polymer

FIGURE 3. Optimized pore structure containing H_2 for a representative polymer through DFT calculation. The inset represents a unit cell of the polymer.

adsorption as the function of hydrogen loading for a representative polymer containing a non-C functional group. The value of ΔH_{ads} was obtained from the adsorption isotherm data measured at the temperatures of 77 K, 87 K, 197 K, 273 K, and 297 K. At low hydrogen coverage with less than 5 H_2 /polymer unit, the ΔH_{ads} has the values of 6 kJ/mol to 7 kJ/mol. The absolute value, however, decreases quickly with increasing hydrogen loading. Although detailed theoretical modeling and characterization are needed for more accurate interpretation, we postulate such change is the result of spreading hydrogen from tighter binding sites closer to the framework wall to less confined space at the center of the cavity. The preliminary pair-distribution function calculation also supports such a hypothesis.

The porous polymers we prepared are generally amorphous without well-defined crystal structures.

FIGURE 4. Measured Isostatic Heat of Adsorption at Different H_2 Loading for a Representative Polymer

Since the micropores are constructed by covalent bonds of light elements, it is possible to pelletize the polymer powder to a higher material density without affecting the overall surface area, thereby substantially increasing the volumetric capacity. We tested a number of our polymers by compressing them under the pressure up to 50,000 lb/in². We found that such approach can lead to a 3 to 5 time increase of adsorbent packing density without significantly reducing SSA. For example, the polymer with 5% hydrogen gravimetric uptake capacity has a loose-powder packing density of ~0.2 kg/L. Increasing the packing density by a factor of 4, we could achieve an excess volumetric capacity of 0.04 kg H_2 /L adsorbent. At present, we still have a number of engineering issues in pelletizing polymers. We plan to continue to explore this pelletizing approach as a method of improving volumetric capacity.

Conclusions and Future Directions

In summary, we prepared over 50 porous polymers from three structural categories in FY 2009. We investigated their surface properties and hydrogen storage capacities in addition to their isosteric heats of adsorption. We also explored the volumetric density enhancement via pelletization based on compressibility of the polymers. Parallel to material development, we carried out computational modeling and advanced characterization for better understanding of the polymer-hydrogen interaction. Our effort for future study will be focused on the following areas:

- Improve H_2 -adsorbent interaction (uptake capacity and ΔH_{ads}) through pore size control and rational design.
- Explore new synthesis methods for metal-containing polymers and to investigate structure-heat of adsorption correlations.

- Refine modeling on H₂-adsorbent interactions, provide guidance to the polymer design.
- Investigate the kinetics and transient properties of hydrogen adsorption over polymers.
- Collaborate with HSCoE on structural and mechanistic studies via advanced characterization (NMR, neutron scattering, etc.).

FY 2009 Publications/Presentations

1. “Hydrogen storage through nanostructured polymeric materials” Di-Jia Liu, Shengwen Yuan, Brian Dorney, Scott Kirklin, Suhas Niyogi, Shengqian Ma, Ricky Regalbuto, Peter Zapol, Jiangbin Xia, Zhuo Wang & Luping Yu, Presentation ST-27, DOE Hydrogen Program Annual Merit Review and Peer Evaluation Meeting, Arlington VA, May 21, 2009.
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IV.C.1g Enabling Discovery of Materials With a Practical Heat of Hydrogen Adsorption

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Project End Date: February 28, 2010

Objectives

- Development and testing of new materials with high H₂ storage density and appropriate enthalpy of hydrogen adsorption.
- Development of enabling technologies for H₂ storage materials development.
 - Accurate, predictive computational methodologies for new materials discovery and mechanistic understanding.
 - Characterization tools for accurate H₂ storage measurements.

Technical Barriers

This project addresses the following technical barriers from the Storage section (3.3.4.2) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) System Weight and Volume
- (C) Efficiency
- (P) Lack of Understanding of Hydrogen Physisorption and Chemisorption

Technical Targets

The project team is conducting fundamental computational and experimental studies of hydrogen storage in carbon-based materials. Insights gained from these studies will be applied toward the design and synthesis of hydrogen storage materials that meet the following DOE 2010 hydrogen storage targets:

- Cost: \$4/kWh net
- Specific energy: 1.5 kWh/kg
- Energy density: 0.9 kWh/L

Accomplishments

- Predictive computational modeling has revealed that crystalline BC₃ is an attractive target material for hydrogen storage. Unlike graphite, chemisorption of hydrogen in BC₃ provides a chemical driving force for H₂ penetration into the lattice.
- The energies of hydrogen diffusion of chemisorbed hydrogen in BC₃ were calculated, showing that hydrogen diffusion on the surface is unlikely at moderate temperatures.
- While the bond dissociation energies of chemisorbed hydrogen in BC₃ suggest that hydrogen binding may be irreversible at high levels of hydrogenation, our computational modeling suggests a path forward by incorporating substitutional nitrogen atoms in the lattice. The average absorption energies for materials that incorporate nitrogen are significantly lower.
- Our experimental capabilities were enhanced to allow the use of pure fluorine for the synthesis of graphite intercalation complexes (GIC). 1st stage GIC, containing fluoride anions, were prepared using pure F₂ and characterized for hydrogen storage capacity and heat of adsorption.
- New synthetic strategies for the preparation of high-surface-area templated boron-doped carbon have been developed.

Introduction

An efficient, cost-effective hydrogen storage system may well be an enabling technology for the widespread introduction of hydrogen fuel cells to the domestic marketplace. We are collaborating with partners in the HSCoE to identify, synthesize, and test novel materials that exhibit heats of adsorption of hydrogen superior to

known materials. This involves predictive computational modeling, materials synthesis, and advanced methods of hydrogen adsorption characterization.

Approach

The project approach is designed to enable and execute discovery of materials with “practical heats” of hydrogen adsorption. These practical heats are hydrogen adsorption enthalpy ranges which allow for the charging and discharging of hydrogen storage materials at near-ambient temperatures and reasonable hydrogen pressures (i.e. 3-100 bar). Our approach utilizes the development of general quantitative computational models for new materials discovery. The accuracy of these methods is very important in order to realize a more practical overlap between computational and experimental work (e.g. modeling the mechanism of hydrogen spillover). Ultimately, the goal is to translate our predictive computational modeling to development and testing of new H₂ storage materials. Our current, novel hydrogen storage materials development is based upon theoretical predictions of high H₂ storage density and enthalpy for boron-doped carbon materials. Once well-characterized samples of the potential hydrogen storage materials have been synthesized, accurate measurement techniques are employed to obtain hydrogen isotherms and heats of adsorption. Advanced techniques such as correction for helium adsorption effects on H₂ isotherms may be employed as necessary.

Results

Computational Modeling of Hydrogen Storage Materials

Recent results by Zhang and Alavi suggest that if H₂ molecules are placed inside the lattice of BC₃, they will undergo nearly spontaneous dissociative chemisorption with formation of C-H bonds at the carbon atoms adjacent to boron [1].

There are literature reports that BC₃ has been synthesized experimentally by reacting BCl₃ with benzene at 800°C via chemical vapor deposition [2]. The balanced reaction scheme is as follows:

Our calculated lattice spacing of BC₃ is in good agreement with the experimental value (calculated 6.79 Å vs. experimental 6.84 Å). AB stacking of the BC₃ layers appears to be the most stable structure, but this has not been resolved experimentally. Our molecular orbital analysis indicates that the empty *p_z* orbital of B, which is perpendicular to the BC₃ plane, overlaps with the σ -orbital of H₂, the highest occupied molecular orbital, leading to electron transfer from H₂ to BC₃ and H₂ bond dissociation.

A key question is whether H₂ molecules can penetrate the narrow interlayer spaces of crystalline BC₃. Our minimum energy path calculations indicate an interlayer space opening (Figure 1) upon reaction with hydrogen, which substantially reduces the activation energy. Thus, in confirmation of Zhang & Alavi's findings, H₂ should undergo an almost spontaneous dissociation in BC₃ without the need of a catalyst. The estimated barrier for recombination of the chemisorbed H atoms to form gas-phase H₂ is approximately 0.5 eV.

We next studied the energy barriers to migration of chemisorbed hydrogen in BC₃ by first placing C-H bonds in selected positions on a sheet of BC₃. The barriers were then estimated by calculating the energies of moving a hydrogen atom from one carbon atom to another carbon atom in the plane. Several site migrations were evaluated: 1 to 2 (movement to adjacent carbon), 1 to 3 (movement to a site two carbon atoms away in the same ring), and 1 to 4 (movement across the ring). The results indicate that the lowest barrier (0.5 eV) is observed for a 1 to 2 migration. The barriers for the 1 to 3 and 1 to 4 migrations were calculated to be 1.3 and 0.8 eV, respectively.

The absorption of hydrogen in BC₃ leads to a range of energies, depending on the concentration of hydrogen in the hydrogenated material. We find that higher hydrogen concentrations lead to higher the average absorption energies (Figure 2). This suggests that at high hydrogen concentrations, the hydrogen binding may be irreversible. Fortunately, an avenue for moderating the

FIGURE 1. Illustration of individual points and energy changes during the minimum energy path for hydrogen entry into the BC₃ interlayer space and subsequent dissociative chemisorption.

FIGURE 2. Calculated values for the average absorption energy of hydrogen in BC_3 as a function of the hydrogen concentration.

absorption energies may be possible by incorporating other atoms in the material. The addition of nitrogen to the layered BC_3 , illustrated in Table 1, results in a decrease in the hydrogen absorption energies. While the average absorption energy of hydrogen in H_3BC_3 is $-0.83 \text{ eV}/\text{H}_2$, the average absorption energies for materials that incorporate nitrogen are significantly lower.

TABLE 1. Calculated average absorption energy of hydrogen in BC_3 and nitrogen-incorporated BC_3 .

Formula	Average Absorption Energy
H_3BC_3	$-0.83 \text{ eV}/\text{H}_2$
$\text{H}_3\text{B}_{0.75}\text{C}_3\text{N}_{0.25}$	$-0.60 \text{ eV}/\text{H}_2$
$\text{H}_3\text{B}_{0.5}\text{C}_3\text{N}_{0.5}$	$-0.37 \text{ eV}/\text{H}_2$

Synthesis and Hydrogen Storage Testing of Graphite Intercalation Complexes

We have been engaged in a study of the adsorption of hydrogen by fluoride-containing GICs. This was motivated by previously reported computational modeling that suggested a substantial interaction of molecular hydrogen with fluoride ions. Unfortunately, our experimental results have indicated that despite the observation of high hydrogen adsorption enthalpies, the as-produced GIC did not lead to substantial hydrogen storage densities due to the low surface area and low pore volume of the GIC. Therefore, we brought the investigation of GIC for hydrogen storage to a close in the second quarter of Fiscal Year 2009.

Results reported in the past year demonstrated that 2nd stage graphite fluoride compounds demonstrated high heats of adsorption, but also had low surface

areas and hydrogen capacity. Therefore, in FY 2009 we expanded our experimental capabilities to include the use of 100% fluorine in the preparation of GIC. We demonstrated that 1st stage graphite intercalates of fluoroanions could be obtained by employing pure rather than diluted F_2 in the co-intercalation chemistry with BF_3 into graphite. While our prior synthesis of 2nd stage GIC resulted in a large increase in the surface area of graphite from $15 \text{ m}^2/\text{g}$ to $70\text{--}120 \text{ m}^2/\text{g}$, additional surface area expected for the 1st stage GIC did not result from our new materials (Figure 3). The low surface area contributes to very low hydrogen adsorption at near-ambient temperatures, despite a heat of adsorption as high as $14 \text{ kJ}/\text{mol}$ at low coverage (Figure 4).

In an attempt to increase the surface area of the GIC, we employed graphitic host materials with higher native surface area. The repetition of the 1st stage C_xBF_4 GIC synthesis and activation was carried out with higher surface area graphite fibers. The resulting material provided H_2 adsorption performance comparable to

FIGURE 3. Elemental analysis and surface areas of 1st and 2nd stage GIC.

FIGURE 4. Isosteric heat of adsorption for hydrogen on 1st stage GIC.

the carefully activated graphite C_xBF_4 and 2nd stage analogs. Following the analysis, it became apparent that the graphite fiber precursors were not 100% graphitic, thus detracting from their overall potential capacity; additionally it is possible that a portion of the graphitic plates are capped, precluding their proper intercalation.

Because accessibility of H_2 to the opened galleries is believed to be the primary challenge in relation to the current materials, it was suggested that single-wall nanotube (SWNT) carbon be employed as a material that inherently possesses exceptional accessibility of gases to the annular zones between packed nanotube bundles. Knowledge exists around the fluorination of nanotubes and even suggests that some fluorinated sites possess a relatively high ionic character; [3] however, there do not appear to be any reports of utilizing this apparent ionic character to complex Lewis acids. Thus, we repeated the BF_4^- intercalation using a SWNT carbon as the host material. The GIC synthesis was conducted using 20% fluorine because of concerns regarding the high surface area and reported reactivity of the SWNT substrate towards oxidizers. The intercalation of the SWNT was verified by tensimetric uptake of reactant gas, as well as direct observation of shifts in the radial breathing modes in the Raman spectrum.

The oxidizing content of the material obtained by iodometric titration was very close to the stoichiometry of $C_{10}BF_4$ obtained from elemental analysis. The material activated at 50°C gave a H_2 uptake of 0.24 wt% H_2 @ 100 atm. and 25°C (with a low isosteric heat of <8 kJ/mol H_2). Activation at 100°C did not change the oxidizing capacity of the material, but dramatically improved the isosteric heat of adsorption (0.24 wt% H_2 @ 100 atm and 25°C; isosteric heat ~11-12 kJ/mol H_2). However, this enhancement does not exceed the performance of the precursor, except with a slight advantage in isosteric heat performance, which is further evidence that the fluoride ion is beneficial to the adsorption of H_2 .

Synthesis and Hydrogen Storage Testing of Boron-Doped Carbon Materials

Starting in the second quarter of FY 2009, we have begun investigation of novel forms of high-surface-area, boron-substituted carbon materials for hydrogen storage. This work is being performed in collaboration with Penn State University. However, there are unique aspects of materials preparation that will be pursued independently in our project.

As part of our collaboration with the group of Prof. Chung at Penn State, we have spent considerable time and effort to measure hydrogen isotherms at a variety of temperatures on several samples of boron-substituted carbon. A BC_x substrate (designated HPA18-500; surface area ~700 m²/g), reported to contain 7 atomic % boron, was analyzed by hydrogen isotherms at multiple

temperatures to obtain more accurate isosteric heat values. The new data clearly shows a fairly uniform heat of about 10-11 kJ/mol- H_2 .

Based upon the H_2 adsorption results from the BC_x material obtained from Penn State, it is apparent that producing a material with significantly higher surface area is required in order to make a valid comparison with model materials (i.e., activated carbons) and maximize the hydrogen adsorption capacity. Our initial concept for generating materials with higher surface area and microporosity is to employ a templating process as described in the literature [4]. We have begun this study by using a liquid precursor for the carbonization (boron phenylacetylide) developed by the Penn State group [5].

Conclusions and Future Directions

In summary, our studies suggest that the fluoride ion is positively affecting the energy of interaction of hydrogen with GIC. Unfortunately, the hydrogen adsorption capacities are limited. Although difficult to prove absolutely, the following are possible causes for the lack of hydrogen storage performance. These ultimately lead to the conclusion that there is reduced accessibility of H_2 to the intercalated fluoride ions and low effective surface area:

- 1st stage GIC are more likely to form considerably less ionic, more covalent C-F bonds upon activation, which will affect overall hydrogen storage performance and planarity of the graphene sheets.
- The ions employed as the pillaring agents (i.e., BF_4^-) are mobile and may form the least energetic domains by clustering, thus reducing the desired porosity. It is noteworthy that the synthetic design of the pillared intercalates relies upon the ability to eject the Lewis acid (i.e., BF_3) at a relatively low temperature in order to minimize covalent C-F formation; this effect inherently enhances the mobility of the ions, allowing them to easily aggregate into isolated domains.
- Because of the use of F_2 in the preparation of materials, it is possible that the edges of the graphite sheets can be heavily fluorinated, reducing their accessibility.
- The insertion of the relatively heavy BF_4^- pillaring group provides gravimetric dilution of the hydrogen storage capacity, in addition to physically crowding the galleries (especially for 1st stage materials); when some of the best H_2 adsorption data is normalized to the absolute carbon content, it actually performs quite favorably in comparison to model adsorbents.
- The application of proper activation (selective and uniform removal of evenly spaced Lewis acid groups) of materials is also an area that requires considerable attention, as it potentially may impact each of the above effects.

Future Directions

- Complete synthesis of boron-doped carbon precursor materials and study decomposition pathways.
- Selection of optimal templates for maximizing surface area and micropore volume of template carbons.
- Detailed parametric study of the carbonization reactions of boron-containing precursors in suitable templates, focusing on maximizing surface area, microporosity, and boron atom retention.
- Hydrogen adsorption testing of high-surface-area templated boron-doped carbons.

FY 2009 Publications/Presentations

1. Dynamics of Hydrogen Spillover on Carbon-Based Materials. Xianwei Sha, M. Todd Knippenberg, Alan C. Cooper, Guido P. Pez and Hansong Cheng; *J. Phys. Chem. C*, **2008**, *112* (44), 17465–17470.
2. Hydrogen Absorption and Diffusion in Bulk α -MoO₃. Xianwei Sha, Liang Chen, Alan C. Cooper, Guido P. Pez and Hansong Cheng; *J. Phys. Chem. C*, **2009**, *113* (26), 11399–11407.
3. “Enabling Discovery of Materials With a Practical Heat of Hydrogen Adsorption”, presented at the DOE HFCIT Annual Merit Review, May 2009.

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5. T. Chung, *et al.*, *J. Am. Chem. Soc.* **2008**, *130*, 6668.

IV.C.1h Optimizing the Binding Energy of Hydrogen on Nanostructured Carbon Materials through Structure Control and Chemical Doping

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Project End Date: January 31, 2010

Objectives

Design and synthesize sorbent materials with optimized binding energies which meet DOE 2015 hydrogen storage targets. Specific efforts include:

- Pore size control
- Surface area increase
- Metal doping of microporous carbon materials
- B doping of microporous carbon materials

Technical Barriers

This project addresses the following technical barriers from the Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) System Weight and Volume
- (B) System Cost
- (G) Materials of Construction
- (P) Lack of Understanding of Hydrogen Physisorption and Chemisorption
- (Q) Reproducibility of Performance

Technical Targets

Enhanced Hydrogen Storage in Microporous Materials:

This project focuses on developing a microporous carbon with controlled pore diameter, pore volume and chemical doping. The goal of this research is to develop microporous carbons with the appropriate binding energies to meet the DOE 2015 hydrogen storage targets of:

- Cost: \$4/kWh net
- Specific energy: 1.8 kWh/kg
- Energy density: 1.3 kWh/L

Table 1 shows progress towards meeting the technical targets set for this project.

TABLE 1. Progress Towards Meeting Technical Targets for Storage

Characteristic	Units	Revised 2015 DOE System Targets for H ₂ Storage	Duke 2009 Materials Status
wt%		5.5 wt%	~6 wt% at 77 K, 7 MPa
Volumetric Capacity	g/L	40 g/L	42 g/L*
Binding Energy	kJ/mol	NA	8.1

NA - not applicable

*assuming density = 0.7 g/ml

Accomplishments

- Developed simple methods that could produce inexpensive hydrogen storage materials with specific energy densities above the DOE 5.5 wt% system target.
- Obtained porous carbons with variable pore diameters (including micropores with diameter 1-3 nm) from the thermal treatment of Poly(ether ether ketone) (PEEK) under CO₂ and steam environments; this is important because porous carbons with a large numbers of micropores and high surface areas have been proposed to be best for H₂ storage.
- Obtained a series of samples with high surface area (>3,000 m²/g) and high microporosity (improved from previous materials with specific surface areas ≤250 m²/g).

- Developed materials that are predicted to have ~6 wt% at 100 K, 7 MPa (70 bar) which corresponds to a 42 g/l volumetric capacity. It should be noted that this is a material storage capacity and not a system storage capacity. The material storage capacity will likely need to be significantly higher than this value to achieve a system storage capacity of 5.5 wt% and 40 g/L.
- Complimentary H₂-nuclear magnetic resonance (NMR) measurements showed >6 wt% storage at 120 K and 10 MPa. These results suggest that materials with large surface areas and optimized small diameter pores may be able to meet DOE hydrogen storage targets at temperatures higher than 77 K, decreasing the cost, weight and volume of the system.
- Optimized pore size materials showed higher binding energy (8.1 kJ/mol) to hydrogen molecules.
- Developed methods for successfully doping this high surface area porous carbon with variable amounts of B and Pd; these are important for binding energy tuning and spillover studies, respectively.
- Produced materials to evaluate the ability of potassium hydroxide (KOH) to improve pore volumes while conserving pore diameters.

Introduction

Nano/microporous carbons are a unique class of materials that are both safe and low in cost relative to many of their storage counterparts. The primary approach of this group over the past year involved the thermal treatment of a high temperature polymer, PEEK, under CO₂ and steam environments. It was found that these methods reliably produce promising porous material with uniform pore diameters tunable to below 1 nm. These porous carbons derived from PEEK had both high surface area (>3,000 m²/g) and impressive hydrogen storage capabilities (~6 wt% at 7 MPa).

Approach

- Develop a simple, safe and cheap method for the preparation of doped and undoped meso and microporous carbon materials with high surface areas.
- Control the pore sizes for optimized H₂ binding energy. This is accomplished from the controlled oxidation of polymeric precursors under well-controlled thermal and chemical conditions. More specific approaches include:
 - Utilize controlled oxidation to increase the number and volume of micropores while increasing surface area.

- Variably incorporate dopants into various porous carbon precursors for the preparation of B and Pd doped microporous carbon materials.

Results

A porous carbon with high surface area and tunable pore size was achieved by thermally treating PEEK under CO₂ and steam environments. The products of both treatments yielded porous materials consisting primarily of carbon, with very little oxygen content as indicated by X-ray photoelectron spectroscopy (XPS, Figure 1). In both cases, this was true even after

FIGURE 1. XPS of (a) PEEK-CO₂-9-80 and (b) PEEK-ST-9-91. Both spectra show that the porous carbon products derived from PEEK are nearly pure carbon materials.

extensive thermal treatment and thus at high surface areas; Figure 1 shows samples made using A) CO₂ and B) steam and having surface areas of 3,103 m²/g and 2,368 m²/g, respectively. This is an important aspect of these materials, as significant oxygen or other non-carbon content would change the H₂ binding energy and likely decrease the gravimetric density of the porous carbon products. Also, this fact is important for doping processes, as large oxygen contents would contribute to the formation of boron oxide and palladium oxide, both of which can interfere with their advantageous functions to H₂ sorption. As such, the H₂ sorption profiles of these pure carbon materials were investigated and compared to other pure and doped carbon materials both within and outside the DOE Hydrogen Sorption Center of Excellence in Table 2. It is evident that these materials are among the most promising and could be important in the future of H₂ storage applications. Gravimetric data of 3.7 wt% (26 g/l volumetric capacity) was demonstrated at 77 K and 2 bar (0.2 MPa); represents a 54% improvement over last year's maximum H₂ gravimetric uptake of ~2.4 wt%. Also of interest to these measurements was the fact that these large H₂ uptake values corresponded to large amounts of H₂ in pores as estimated by H₂-NMR from our partners at University of North Carolina (UNC). In many cases, more than 40% of the H₂ adsorbed resided in the pores. Furthermore, these materials have very high net capacities (~99% assuming a variable temperature fuel cell at 3 bar). This means that nearly all the H₂ stored in these products can be recovered and used as fuel. More detailed relative H₂ pore population measurements are presently being done by our partners at UNC.

In addition to the impressive H₂ sorption characteristics of these pure carbon materials, it was believed that they are very well suited for doping; B and Pd were investigated as specific areas of interest for doping because of their proposed binding energy enhancement and spillover capabilities, respectively. It is hoped that, by utilizing the enhancements of each dopant, a material can be produced in a scalable fashion that can be used to meet the DOE system targets. As such, two methods for producing doped porous carbon materials were designed. As can be seen in Figure 2A and 2C, variable amounts of B and Pd were successfully doped into our high surface area porous carbon. It is crucial that these doping procedures not introduce large amounts of oxygen to the resultant

TABLE 2. Porous carbon products derived from PEEK have large surface areas and impressive gravimetric and volumetric H₂ sorption data when compared to other pure and doped carbon materials. Materials in blue are produced using CO₂ whereas those in red are produced using steam. Other materials used for comparison are designated in maroon.

Material	BET SA (m ² /g)	H ₂ wt%	Volumetric Capacity (g/L)	% H ₂ in Micropores
PEEK-CO ₂ -9-1	524	1.6	11	45
B/C ¹	780	~1.6 (at 77 K 1.2 bar)		
PEEK-CO ₂ -9-5	700	2.0	14	
CMK-1 ²	1,788	2.19 (77 K, 1 bar)		
PEEK-CO ₂ -9-26	1,027	2.2	15	37
PEEK-ST-9-47	1,207	2.3	16	42
PEEK-ST-9-20	1,294	2.4	17	48
PEEK-ST-9-70	1,956	3.0	18	
AX-21 ³	3,300	~3.0 (77 K, 2 bar)		
PEEK-CO ₂ -9-80	3,103	3.7	26	28
Corncob ⁴	3,500	~5 (at 77 K, 20 bar)		

1. T.C. Mike Chung; DOE Annual Merit Review Presentation, June 2008
2. Gao, L.; International Journal of Hydrogen Energy 33 (2008) 116 – 123
3. Measured at the National Renewable Energy Laboratory
4. Pfeifer, P.; RC 1 TT Presentation

FIGURE 2. XPS data showing porous carbon materials doped with various amounts of B and Pd as displayed in A and C respectively. These spectra display that the products contain very little oxygen and consist primarily of dopant material and carbon. Spectra B and D respectively display that B and Pd exist in their elemental forms rather than as oxides. This is important for boron's enhancement of binding energy and for Pd's spillover characteristics to be realized.

materials, as was previously stated. Figure 2B and 2D demonstrate that the processes designed and utilized here produce products that are primarily oxide free. As such, tunable doping procedures which conserve surface area and porosity have been achieved herein. Our partners at the National Renewable Energy Laboratory and UNC are presently testing the H₂-binding energies and uptakes of these materials.

Conclusions and Future Directions

By varying the thermal treatment time and doping level, the pore diameter, surface area and thus binding energy can be tuned to produce materials which demonstrate great promise for H₂ storage. This group demonstrated a highly microporous carbon (pore diameter 1-3 nm) with very exciting surface area and H₂ binding energy (3,103 m²/g and 8.5 kJ/mol, respectively). Future work will include:

- Further high surface area B and Pd doped porous carbon production and analysis.
- PEEK thin films.

- Further PEEK thermal trials at different temperatures.
- Further contributions of material for spillover studies for Dr. Yang (University of Michigan) and H₂-NMR calibration at UNC.

FY 2009 Publications/Presentations

1. “H₂ Storage in Microporous Carbons from PEEK Precursors”, Thomas P. McNicholas, B.J. Anderson, Alfred Kleinhammes, Anmiao Wang, Yanqin Wang, Yue Wu, Jie Liu (In Preparation, 2009).
2. “Single-Walled and Few-Walled Carbon Nanotubes: From Synthesis to Applications”, Staten Island College, City University of New York, May 1, 2008.

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IV.C.1i Nanoengineering the Forces of Attraction in a Metal-Carbon Array for H₂ Uptake at Room Temperature

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Objectives

- The primary objective is to design and produce nanoengineered carbon-metal media which is capable of achieving: 1) 65 g/L; 2) 7.5 wt% storage of hydrogen at near-ambient temperatures; 3) superior thermal management; 4) high energy efficiency; 5) 5 kg fill in 3.3 minutes; 6) 2,000 fill cycles; 7) low cost media less than \$67 per kg H₂ stored; 8) 3 to 100 bar delivery; 9) near-ambient

temperatures; and 10) avoid large temperature swings to obtain complete H₂ delivery.

- Develop a graphene slit-pore scaffold using very low cost ingredients to be within DOE cost targets.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen, Fuel Cells & Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) System Weight and Volume
- (B) Cost
- (C) Efficiency
- (E) Charging/Discharging Rates
- (J) Thermal Management
- (P) Lack of Understanding Hydrogen Physisorption and Chemisorption

Technical Targets

A. Develop nanoengineered graphene scaffolds (see Table 1) with metal atom functionalization for multilayer dynamical adsorption into the slit pore; B. The graphene-metal scaffold is readily made from low-cost graphite, sulfuric acid with common metal atom intercalants, and scalable fiber spinning to meet DOE cost targets; C. & E. The physisorption process has no energy barrier, thereby minimizing energy consumption, and no kinetic barrier for fast fill; J. Graphene has high thermal conductivity; hence use fibrous media to benefit from this; P. The uptake into the engineered nanopore is understood by a thermodynamic model.

TABLE 1. Nanoengineered Graphene Scaffolds

Storage Parameter	Units	2010 System Target	FY 2008 Nanoengineered Graphene (media only)	FY 2009 Nanoengineered Graphene
Specific Energy	kWh/kg (wt% H ₂)	2.0 (6 wt%)	Calculated 2.5 kWh/kg 7.5 wt% excess capacity delivered	0.8 kWh/kg 1.4 wt% G 2.4 wt% CNT
Volumetric	kWh/L g/L	1.5 45	Calculated 2.2 kWh/L 65 g/L excess capacity delivered	Density = 1.3 18.2 g/L G 30 g/L CNT
Desorption Temp.	°K	2 bar min	Calculated ≥253	>77
Plateau Pressure	bar	2 bar min	100 bar fill/3 bar out	Measured at 2 bar

G – graphene; CNT – carbon nanotube

Accomplishments

1. We produced graphene nanoribbons and used a scalable industrial-type spinning process, creating an entirely new type of fibrous nanoengineered slit pore H_2 storage media (Figure 1).
2. We created an engineered nanospace graphene slit pore scaffold and demonstrated enhanced H_2 storage properties similar to those for CNTs (Figure 2). This demonstrates our ability to transfer our extensive experience with CNT chemistry to nanoscale graphene chemistry.
3. We developed the concept of dynamic multilayer adsorption (Figure 3) with electrostatic enhancement for H_2 uptake near room temperature, with calculated excess adsorption of 65 g/L and 7.5 wt% (media only). Key steps: a) measured the enhanced H_2 uptake effect at 77 K for a graphene slit pore; and b) successful production of a charged donor-acceptor complex of sodium on CNTs (Figure 3, bottom).

FIGURE 1. Graphene Nanoribbon Fibers. An individual graphene nanoribbon is seen by transmission electron microscopy (TEM). These have been made into fibers by scalable spinning techniques also used for CNT, observed by scanning electron microscopy (SEM). The fiber responds to oleum expansion and crosslinking, just as for CNT. After swelling in oleum (fuming sulfuric acid), the methylene di-aniline compound binds to adjacent graphene surfaces and provides a chemically bonded molecular spacer holding the graphene sheets apart to form a slit pore. If no crosslinker is added, then the nanopores collapse and the fiber shrinks when the oleum is extracted (observed by optical microscopy).

Introduction

We have made a major shift in our goals from spun fibers of carbon nanotubes to fibrous graphene scaffolds, using a material which was not even in the nanotechnologist's toolbox at the onset of this project [1]. As one of the leaders in nanoscale graphene chemistry, this appeared to be an opportunity for us to move to an ideal material to make a nanoengineered slit pore adsorption media, using very low-cost precursor materials. Creating alternating charged layers using metal atoms on graphene electrostatically attract H_2 bringing high density hydrogen storage up to room temperature (RT).

Approach

All the methods necessary to create low-cost metal-intercalated graphene scaffolds for hydrogen storage will leverage our extensive expertise developed for CNT scaffolds.

FIGURE 2. Enhanced Uptake H_2 also Observed in Graphene. Two oleum expanded graphene samples, one with diphenyl crosslinker (cross) and one with t-butyl aniline spacer (triangle), pre-baked at 500 and 700 C. Sunburst symbol = average of all four graphene measurements; this lies nearly on the same slope as the many measurements on nanoengineered CNT fibers (small diamonds) [Publication: 1.85x steeper slope vs. "Chahine's rule" for activated carbon, using only 2 bar H_2 uptake pressure—Leonard-Tour 2009]. Squares are graphene treated with diphenyl crosslinker, but without oleum expansion of the slit pores, and hexagon symbols are raw graphene starting material as controls. Unexpanded graphene samples fit the standard Chahine rule slope of 2 wt% per 1,000 m^2/g Brunauer-Emmett-Teller surface area [3] typical of activated carbons; lacking the expanded nanopores, this shows an absence of the enhancement effect. (All measurements by the National Renewable Energy Laboratory [NREL].) Similar enhanced H_2 uptake on sp^2 carbon surfaces: observed [4], theory [5].

- 1) Develop sources of graphene and graphene nanoribbons [publ. Kosynkin-Tour 2009] as a new low-cost slit-pore media (Figure 1).
- 2) Prop open graphene sheets to make engineered nanospaces.

FIGURE 3. Dynamic Multilayer Adsorption (DMA) with Electrostatic Enhancement for H_2 Uptake at RT. This illustrates the concept of nanoengineered alternating charged slit pore with (+) sodium (or potassium) and (–) graphene layers that establishes the attractive electrostatic potential via dipole induced dipole forces on H_2 . This donor-acceptor complex (DAC) provides the additional free energy to activate thermodynamic compression at RT, which considerably enhances the attractive potential compared to that of previous work [5]. The “X” substitutional atom (e.g., boron) in the graphene lattice is chosen to enhance the charge separation. This design makes entropy our friend, which prevents site specific binding of the H_2 to the metal atoms. The dynamic H_2 uptake (rather than static attachment to specific sites) considerably reduces enthalpy needed for uptake and consequent heat management problems, increases efficiency, and considerably reduces the range of temperatures necessary for desorption. For free energy $-\Delta F = 13$ kJ/mol, the (fugacity corrected for non-ideal gas behavior) equilibrium constant is 35, so that an external fill pressure of 100 bar corresponds to an internal “pressure” of 3.5 kbar, and the calculated electrostatic energy from the charge separation is sufficient [2] achieve the needed potential energy. Unlike static multilayer adsorption, the dynamic motion here causes all hydrogens to experience the same free energy of adsorption. At the bottom is a Raman spectrum of a sodium DAC. A large number of separated atoms donate electron charge to the CNT pi cloud (similar results obtained for potassium). The excitation wavelength is 785 nm. The appearance of the third resonance Raman feature at $1,510\text{ cm}^{-1}$ Kohn anomaly [6] can only occur if the electron donation is so large as to raise the Fermi level into the conduction band, and also provide a large downshift the G-peak [7] which also correlates with electron donation.

- 3) Develop spinning methods for graphene to make fibrous media (Figure 1).
- 4) Verify $\sim 2\times$ enhancement in hydrogen uptake compared to typical activated carbons (Figure 2).
- 5) Develop alkali metal functionalization and diagnostics to show charge transfer.
- 6) Develop concept of alternating charge slit pore for enhanced uptake of H_2 near RT.

Results

Single sheet graphene was developed as a new material for nanospace engineering for enhanced H_2 uptake; graphene nanoribbons [publ. Kosynkin-Tour 2009] and spinning fibers from them (Figure 1).

Cost analysis: Approximate cost of raw materials in bulk: graphite \$550/tonne, sulfuric acid \$100/tonne, sodium \$500/tonne, ammonia - \$200/tonne (solvent for sodium) etc. for a raw materials cost of $\sim \$1.40/\text{kg}$ and $\$1/\text{kg}$ to $\$3/\text{kg}$ for spinning the fiber; therefore projected materials cost should be close to the DOE system target of $\$67/\text{kg}$ H_2 stored using the calculated 7.5 wt% uptake.

From CNT to Graphene: Several proppants that worked well for carbon nanotubes as sidewall functional groups, including aryl sulfonates and t-butyl aniline, have now been developed for use with graphene [publ. Lomeda-Tour-2008]. Likewise, methyl di-aniline has proved suitable as a crosslinker to hold open the graphene slit pore. Pyridine functionalization has been demonstrated that will provide a “parking spot” for alkali metals so they are immobilized to prevent aggregation and loss of functionality.

H_2 uptake tests on graphene slit pores shows a similar enhancement in hydrogen uptake compared to typical activated carbons observed for CNT (Figure 2) [publ. Leonard-Tour 2009].

Metal atom intercalation with sodium exhibits a Raman spectrum commensurate with a strong DAC (Figure 3, bottom). DAC is needed to establish alternating charge layers for enhanced electrostatic attraction of the hydrogen into the nanopore.

Designed nanoengineered metal-graphene layered structure with slit pores. A free energy difference of only $-\Delta F = 13$ kJ/mol between the inside/outside the pore (Figure 3, also see [2]) will produce an equilibrium constant of $K = 35$ (corrected for fugacity) that will compress the hydrogen into the graphene pore. This is calculated to achieve the H_2 uptake amounts at near-ambient temperatures indicated above.

Conclusions and Future Directions

- The H₂ compression uptake mechanism is now understood to be a property of nanoporous sp² carbon as shown for both CNT and graphene nanoporous material.
- Expertise in CNT chemistry is successfully applied to graphene to make nanoporous scaffolds.
- An alternating charge layered structure can provide enhanced binding in the slit pore that will lead to high H₂ uptake at near ambient temperatures.
- We plan to transfer the enhanced hydrogen uptake concept of the CNT scaffold to the metal-graphene scaffold so that similar high density H₂ uptake occurs, but near RT.
- We will add metal atom intercalation to parking spots on grapheme.
- Our goal is to demonstrate 45 g/L hydrogen storage at near-ambient temperatures by constructing a metal/graphene structure similar to that of Figure 3 and determining H₂ uptake with pressures of 30 to 100 bar.

Presentations

1. Keynote Speaker Presentation by James Tour; Nanotechnology: The Passive, Hybrid and Active Sides” SERMACS Cope Scholar Symposium, Nashville, TN. (November 2008).
2. Keynote Speaker Presentation by James Tour; Wageningen Symposium on Organic Chemistry: Wageningen, The Netherlands. (April 2 and 4, 2008).

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IV.C.1j Carbon Aerogels for Hydrogen Storage

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Partner Approach

This effort is focused on the design of new nanostructured carbon-based materials that meet the former DOE 2010 targets for on-board vehicle hydrogen storage, including capacity targets of 6 percent hydrogen by weight and 45 grams of hydrogen per liter. Carbon aerogels (CAs) are a unique class of porous materials that possess a number of desirable structural features for the storage of hydrogen, including high surface areas (over 3,000 m²/g), continuous and tunable porosities, and variable densities. In addition, the flexibility associated with CA synthesis allows for the incorporation of modifiers or catalysts onto the surfaces of the carbon matrix in order to alter hydrogen sorption enthalpies in these materials. Since the properties of CAs can be systematically modified (i.e. surface chemistry, pore structure, amount/type of dopant), novel materials can be fabricated that exhibit enhanced hydrogen storage properties. For example, we have used this approach to prepare high surface area CAs that exhibit excess gravimetric H₂ densities over 5 wt% and volumetric H₂ capacities of 29 g/L at 77 K and 30 bar. We are now exploring the design of new H₂ sorbent materials that can store appreciable amounts of hydrogen at reasonable operating temperatures. One such approach, known as hydrogen spillover, involves the dissociative chemisorption of molecular hydrogen on a supported metal catalyst surface (e.g. platinum or nickel), followed by the diffusion of atomic hydrogen onto the surface of the support material. Due to the enhanced interaction between atomic hydrogen and the carbon support, hydrogen can be stored in the support material at more reasonable operating temperatures. While the spillover process has been shown to increase the reversible hydrogen storage capacities at room temperature in metal-loaded carbon nanostructures, a number of issues still exist with this approach, including slow kinetics of H₂ uptake and capacities (~1.2 wt% on

carbon) below the DOE targets. The ability to tailor different structural aspects of the spillover system (i.e. the size/shape of the catalyst particle, the catalyst-support interface and the support morphology) should provide valuable mechanistic information regarding the critical aspects of the spillover process (i.e. kinetics of hydrogen dissociation, diffusion and recombination) and allow for optimization of these materials to meet the DOE targets for hydrogen storage. As an alternative approach to enhanced hydrogen uptake, we are also investigating the functionalization of the skeletal aerogel network with molecular units that can stabilize isolated metal atoms or organometallic species capable of reversibly binding H₂ molecules. The synthesis of aerogel materials allows for the incorporation of different types of metal-binding sites, including phosphorous-, nitrogen-, or sulfur-containing functional groups. This flexibility should allow for the design of new sorbent materials that can bind multiple H₂ molecules at the appropriate binding energies for room temperature storage.

In a parallel effort, we are also designing CA materials as nanoporous scaffolds for metal hydride systems. Recent work by others has demonstrated that nanostructured metal hydrides show enhanced kinetics for reversible hydrogen storage relative to the bulk materials. This effect is diminished, however, after several hydriding/dehydriding cycles, as the material structure coarsens. Incorporation of the metal hydride into a porous scaffolding material can potentially limit coarsening and, therefore, preserve the enhanced kinetics and improved cycling behavior of the nanostructured metal hydride. Successful implementation of this approach, however, requires the design of nanoporous solids with large accessible pore volumes (>4 cm³/g) to minimize the gravimetric and volumetric capacity penalties associated with the use of the scaffold. In addition, these scaffold materials should be capable of managing thermal changes associated with the cycling of the incorporated metal hydride. CAs are promising candidates for the design of such porous scaffolds due to the large pore volumes and tunable porosity of aerogel framework. In addition, the synthesis of CA allows for the dispersion of secondary materials into the carbon matrix that can serve as catalysts or destabilizing agents for the metal hydride and potentially influence the transport properties of the scaffold. For example, we have demonstrated that the incorporation of carbon nanotubes into the CA framework not only improves the thermal conductivity of the scaffold, but may also affect the kinetics of dehydrogenation for certain metal hydrides. This research is a joint effort with HRL Laboratories, a member of the DOE Metal Hydride Center of Excellence (MHCoE). LLNL's efforts

have focused on the design of new CA materials that can meet the scaffolding requirements, while metal hydride incorporation into the scaffold and evaluation of the kinetics and cycling performance of these composites is performed at HRL.

Partner FY 2009 Results

- Improved synthetic methods have been developed for the fabrication of CA scaffolds that possess both large pore volumes ($\sim 5 \text{ cm}^3/\text{g}$) and small average pore sizes ($<20 \text{ nm}$).
- Novel CA-carbon nanotube (CNT) scaffolds (see Figure 1) with improved thermal transport properties were used in the preparation of a CA/ LiBH_4 nanocomposite that showed a decrease in hydrogen desorption temperature relative to bulk LiBH_4 . Metal hydride incorporation and desorption measurements were performed by MHCoe members at HRL Laboratories.
- New aerogel substrates containing functional groups capable of binding and stabilizing organometallic species have been synthesized. For example, high surface area silica aerogels ($750 \text{ m}^2/\text{g}$) containing diphenylphosphine groups have been prepared. Metal incorporation and hydrogen uptake experiments are being performed by Hydrogen Sorption Center of Excellence (HSCoe) members at the National Renewable Energy Laboratory (NREL).
- Methods developed to readily modify surface chemistry of CA substrates for both spillover

materials and metal hydride scaffolds. For example, high surface area CAs with increased oxygen content ($>20 \text{ wt}\%$) have been prepared for testing as spillover substrates. In addition, we have also demonstrated the ability to incorporate destabilizing agents into scaffold materials. For example, scaffolds coated with a thin layer of nanocrystalline titania (TiO_2) have been prepared (Figure 2).

Future Directions

Based on the promising results from FY 2009, we will continue to investigate surface modification of aerogel materials as a strategy for the design of sorbents with improved H_2 uptake. In FY 2009, we developed methods that allowed us to tailor the surface chemistry of the aerogel sorbent. Future work in this area will focus on the design of functionalized aerogels that can stabilize organometallic species capable of reversibly binding multiple H_2 molecules at reasonable operating temperatures. In addition, we will examine the influence of substrate surface chemistry on the capacity and kinetics in spillover materials. These studies will be performed with HSCoe members at NREL and Caltech. For the scaffolding effort, we will continue to focus on the preparation of new CA composite structures that possess the requisite pore structure, transport properties and surface chemistry. In FY 2009, we were able to fabricate CA nanocomposites containing dispersions of CNTs that exhibited enhanced thermal conductivity relative to unloaded CA materials. In addition, we developed methods that allowed for the incorporation of destabilizing agents (i.e. TiO_2) onto the surfaces

FIGURE 1. Scanning electron micrograph of a carbon scaffold composite containing 55 wt% single-walled carbon nanotubes.

FIGURE 2. Scanning electron micrograph of a carbon aerogel scaffold coated with a conformal layer of nanocrystalline TiO_2 (37 wt%).

of the scaffold network. As the structures of these scaffolds continue to evolve, our efforts will focus on the homogeneous incorporation of other destabilizing agents and catalysts, such as Ni or Ti, into these matrices to facilitate the hydriding and dehydriding processes. We will also develop methods for controlling the surface chemistry of the CA to improve the wetting behavior of destabilizing entities, such as Mg, in these materials. Evaluation of the metal hydride scaffolds will be performed by MHCoE members at HRL Laboratories.

FY 2009 Publications/Presentations

1. “High Surface Area Carbon Nanotube-Supported Titanium Carbonitride Aerogels” M.A. Worsley, J.D. Kuntz, P.J. Pauzauskie, O. Cervantes, J.M. Zaug, A.E. Gash, J.H. Satcher and T.F. Baumann, *Journal of Materials Chemistry*, **2009**, *in press*.
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IV.C.1k ORNL Progress within the DOE Center of Excellence for Hydrogen Sorption: Synthesis and Processing of Single-Walled Carbon Nanohorns for Hydrogen Storage and Catalyst Supports

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Project Start Date: 2005

Project End Date: Project continuation and direction determined annually by DOE

Objectives

The overall objective of the project is to exploit the unique morphology, tunable porosity and excellent metal supportability of single-walled carbon nanohorns (SWNHs) to optimize hydrogen uptake and binding energy through an understanding of metal-carbon interactions and nanoscale confinement. Specifically, in the current year, the objectives are to:

- Develop activation processes to nanoengineer sub-nm pores in SWNHs with high binding energy.
- Develop new techniques to Ca-decorate opened SWNHs and test the theoretical predictions of enhanced uptake and smooth coatings.
- To address computationally hydrogen storage in metal-decorated carbons, such as Ca-O-SWNHs and other charged nanostructures, which are designed with high static electric fields in nanoengineered pores or layers.

Technical Barriers

This project addresses the following technical barriers from the Storage section (3.3) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) System Weight and Volume
- (B) System Cost
- (C) Efficiency
- (D) Durability/Operability
- (J) Thermal Management
- (P) Lack of Understanding of Hydrogen Physisorption and Chemisorption

Technical Targets

This project is developing nanoengineered metal-decorated SWNHs for use as effective hydrogen storage media to satisfy DOE system targets. The project is addressing the 2010 system targets of:

- System Gravimetric Capacity: 2 kWh/kg (0.06 kg H₂/kg system)
- System Volumetric Capacity: 1.5 kWh/L (0.045 kg H₂/L system)
- Charging/Discharging Rates: 3 min for 5 kg system fill

Currently, this project has demonstrated gravimetric hydrogen uptakes of SWNHs between 0.6-1.5 wt% at room temperature, ~ 3.5 wt% at 77 K, and ~6.4 wt% at 30 K. The volumetric capacity demonstrated to date is 35 g/L for compressed pellets of decorated, opened nanohorns which is 67% of the 2010 system target. This project also will address the high thermal conductivity requirements required for system charging through incorporation of high thermal diffusivity (2.1 cm²/s) porous aligned nanotube arrays with the nanohorn storage medium.

Accomplishments

- High surface areas: SWNHs were synthesized in gram quantities with pore sizes adjusted to maximize surface area (2,142 m²/g) and increase excess storage (3.5 wt% at 77 K).
- Tunable, small pores: Nuclear magnetic resonance (NMR) confirmed the majority of storage in the

interstitial (~ 0.5 nm) pores on large SWNHs, and in activated pores (<1 nm) in short-SWNHs. These NMR shifts are the highest among all materials studied, indicating storage in very small pores. Work continues to understand the activation process, but is aided by the stability of the nanohorn aggregate structure which is defined at very high temperatures during synthesis.

- Room temperature storage: Undecorated, short oxidized-SWNHs (o-SWNHs) reversibly store significant hydrogen (0.6 wt% at 30 bar) at room temperature, comparable to bridged metal-organic frameworks and Pt-decorated o-SWNHs (1.5 wt% at 100 bar). These “nanoengineered pores” are defined both by the unique nanostructure self-assembled during synthesis, and by the activated pores during oxidation.
- Enhanced Binding Due to Metal Decoration - Doping-Induced Charge Separation - Methods of vapor phase Ca-decoration were developed and found to result in smooth decoration unlike decoration by transition metals which results in small nanoparticles. These results confirm our theoretical predictions, which predict that of all the elements, alkaline earth metals Ca and Sr should have a special ability to coat C nanostructures without clustering while providing sufficient electric field strength to polarize and bind H_2 with 8.4 wt% and 0.4 eV for Ca.

Introduction

SWNHs are carbon nanostructures with a unique morphology with potential for high capacity hydrogen storage media capable of satisfying DOE technical targets. Nanohorns are cone-shaped, atomic-layer-thick nanostructures which contain preferred hydrogen adsorption sites in their tips and have variable internal and interstitial pores that have been shown to contain hydrogen at liquid hydrogen density or higher (Figure 1). They can be functionalized by tailoring their pores and by metal decoration. They can be produced in large quantities, and have been shown to serve as excellent metal catalyst supports for fuel cells and batteries in addition to their potential as sorbents.

The ultimate goal of this project is to make use of SWNH complexes for efficient hydrogen storage media by (a) utilizing their high surface areas effectively to meet hydrogen gravimetric DOE targets, (b) optimizing their geometries for containing high volumetric densities of hydrogen, and (c) increasing their binding strength to hydrogen by metal decoration for ambient condition hydrogen storage application.

FIGURE 1. Aggregates of “short” and “long” single-wall carbon nanohorn aggregates produced by laser vaporization. Schematic representation of individual nanohorns shown.

Approach

Carbon nanohorn aggregates are assembled from the “bottom up” from individual nanohorns. Our approach is threefold. First, the shape of individual nanohorns is tuned during synthesis to find morphologies with adsorption sites and high binding energies (e.g., in the tips of SWNHs). Second, the nanohorn aggregates have innate interstitial pores which can be tuned by oxidative treatments and other processing techniques (heat, compression, etc.). The internal pores and external pores can be investigated separately. Thus, the nanospaces of the pure carbon framework can be engineered to understand and optimize hydrogen storage in these “bottom up” assembled, pure-carbon structures. Third, metals are used to coat or decorate the activated aggregates to explore spillover based storage or store hydrogen directly on the metal coating. This overall approach permits the storage due to engineered nanospaces and that resulting from metals to be explored and tuned separately.

Results

The morphology of the SWNHs was adjusted by tuning the pulse width and energy of the laser used in the carbon vaporization process, producing “large” and “small” carbon nanohorns as shown in Figure 1. The pores responsible for the majority of hydrogen storage in these as-produced and activated (‘opened’) aggregates were compared using an NMR technique by Hydrogen Sorption Center of Excellence partners at the University of North Carolina. The results (Figure 2) revealed that aggregates of ‘large’ nanohorns possess interstitial pores which store significant quantities of hydrogen in sub-nm pores (where small SWNHs do not). The internal and slit pores of the small SWNHs, revealed after oxidation, are the favored sites for hydrogen storage. These results indicate that interstitial pores provide more opportunity as preferred sites for hydrogen storage than previously recognized, and that synthesis conditions should be tuned to optimize the pore volume in these sites.

Efforts on metal decoration of the activated SWNHs concentrated upon processing techniques to attempt Ca decoration. Several processing techniques were implemented to decorate SWNHs with Ca. These included in situ vaporization of Ca during SWNH

synthesis, vaporization of C into Ca vapor, and post-synthesis infiltration of Ca vapor at high temperatures. The latter technique proved successful. High resolution transmission electron microscopy and Z-contrast scanning transmission electron microscopy/electron energy loss spectroscopy (EELS) measurements (Figure 3) were performed to understand whether Ca formed smooth, uniform coatings as predicted by theory. As shown in Figures 3(b) and 3(c), Ca was uniformly distributed within and on the outer surfaces of opened, small SWNHs. EELS measurements confirm that the controlled atmosphere processing utilized in the coating process resulted in insignificant oxidation of the Ca.

Nitrogen surface area measurements of the Ca-coated SWNHs, however, indicated that the Ca coating resulted in a major reduction in surface area (from ~1,200 m²/g to ~300 m²/g) as shown in Figure 4. Since the infiltration process did not have in situ process control during these experiments, significant coating and pore blocking could be expected. Hydrogen adsorption isotherm measurements were performed at 77 K and 0.9 atm to compare the Ca-decorated o-SWNHs with the undecorated o-SWNHs. The isotherms were reversible,

FIGURE 2. NMR measurements (University of North Carolina) revealing the hydrogen stored in sub-nm pores in large and small nanohorns, opened and unopened by oxidation. The shift of peak 2 is greater for smaller diameter pores. The interstitial pores in large nanohorns surprisingly store hydrogen in smaller pores than the internal pores of small nanohorns.

FIGURE 3. Electron energy loss spectra of Ca-decorated SWNHs, showing Ca, lack of O, and map of Ca in an aggregate shown in (b) Z-contrast scanning transmission electron microscopy, high-angle annular dark-field image and (c) scanning transmission electron microscopy bright field image. The Ca appears uniformly distributed in the SWNH aggregate. (G. Duscher, University of Tennessee.)

FIGURE 4. Comparison of hydrogen adsorption measurements at low (0.7 – 2 atm.) pressure and 77 K vs. surface area. The Ca-decorated samples exhibit a higher figure of merit despite greatly reduced surface area.

and the Ca-decorated o-SWNHs isotherms indicated possible capillary condensation. To account for the difference in surface areas between the different samples, a figure of merit was defined as the wt% hydrogen measured per atmosphere hydrogen gas divided by 500 m²/g. Typically at high pressures, high surface area activated carbons often exhibit 1 wt% excess adsorption at 77 K for every 500 m²/g surface area (line in Figure 4, usually obtained at pressures >20 bar). However it is evident that the Ca-decorated o-SWNHs outperform undecorated samples and exceed this metric even at low (~1 bar) pressures, with a figure of merit a factor of 4 higher.

Preliminary measurements on Ca-decorated activated carbons (e.g., AX-21 obtained from Caltech) were performed to extend these measurements to commercial nanocarbons, however the coatings and modest improvements demonstrated are preliminary and will be pursued further.

Conclusions and Future Directions

This project has demonstrated that pore sizes in pure carbon nanohorn aggregates can be tuned 1) during synthesis, and 2) during activation, and that this sometimes results in room temperature binding of up to 1.5 wt% hydrogen. The effects of metal decoration have been demonstrated. Enhanced storage at room temperature in Pt- and Pd-decorated SWNHs were investigated by neutron scattering, and indicate that spillover may be partly responsible. However, metal decoration with Ca has been shown to result in smooth

nanoparticle-free coatings and anomalously high storage, in agreement with our proposed mechanism of *polarization induced by high local electric fields* resulting from the alkaline-earth metal “doping” of C by decoration.

Future work should pursue this highly promising new direction on two fronts. First, work should continue with high-surface area carbons to maintain high surface areas while uniformly coating these materials. For nanohorns the Ca-coating process can be optimized by integrating it as an inherent part of the synthesis process, while for activated carbons in situ process monitoring during infiltration should be implemented. Second, new materials, such as layered organic crystals (e.g., tetracyanoquinodimethane salts) or thin films - with built-in high electric fields and nanoengineered spaces sufficient for hydrogen molecules - should be investigated to capitalize on the same principle employed for the nanohorns.

FY 2009 Publications/Presentations

1. “Single-Walled Carbon Nanohorns for Hydrogen Storage and Metal Catalyst Supports”, David B. Geohegan, Invited Presentation at Solid Storage of Hydrogen (SSH-IP) Workshop, Fodele, Greece, June 10, 2009.
2. “Hydrogen storage in charge compensated organic molecular crystals”, Mina Yoon and Matthias Scheffler, Contributed talk at American Physical Society March Meeting, Pittsburgh, Pennsylvania, March 18, 2009.
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IV.C.1I Enhanced Hydrogen Dipole Physisorption

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Project End Date: January 31, 2010

contributions are not considered as part of this analysis as these depend on the surface area and skeletal density of the sorbent. Inclusion of such a number will typically add ~30% to the values noted below. The contribution to the system weights from the tanks and insulation are not considered in our values whereas the DOE targets for gravimetric and volumetric capacity are targeted on a system's basis of 5.5 wt% (1.8 kWh/kg) and 0.040 kg/L (1.3 kWh/L), respectively.

The best materials we have synthesized/studied to date have a specific energy of 1.91 kWh/kg and a volumetric density of 1.28 kWh/L, measured at 77 K.

Accomplishments

- Completions of synthesis of MOF-177 for neutron scattering studies (that are still in progress).
- Synthesis of intercalated graphites for isosteric heat analysis. These systems are one of the few examples of materials that maintain constant isosteric heat, an important material parameter for designing an engineering system. The isosteric heat in KC24, RbC24 and CsC24 are 9, 11, and 13 kJ/mole H₂ respectively, and unlike most other physisorbents where the heats decay as a function of loading, the values from intercalated graphites are generally constant as a function of loading.
- Improvement to fits of empirical data through modeling of virial equations, yielding improved isosteric heat analysis.
- Synthesis and analysis of a 3 gm batch of Pt loaded super-activated carbon for spillover analysis. All of our previous attempts at determining the extent spillover in carbon systems yielded inconsistent data. We have now concluded that as measured via normal Sieverts volumetric techniques, that any possible enhancement of uptake that might occur through dissociation reactions, is minimal compared to the amount of catalyst weight that is required to initiate dissociation.

Introduction

High surface area-based physisorbents are a class of materials that are closer to engineering viability for high gravimetric density reversible onboard storage applications, than other onboard reversible candidate materials, provided that 77 K is an acceptable temperature at which to store hydrogen. Further optimization of this class of materials will be necessary in order to increase volumetric densities and to offer

Objectives

- Synthesis, analysis, and quantification of surface excess isotherm behavior in high surface area carbon and modified framework structures.
- Establishment of the principle of enhanced dipole physisorption.
- Evaluation of the efficacy of carbon and other high surface area systems as commercially viable hydrogen storage sorbents.
- Overcome specific thermodynamic limitations to hydrogen physisorption, by deepening the potential well for physisorption.

Technical Barriers

This project addresses the following technical barriers from the Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) System Weight and Volume
- (P) Lack of Understanding of Hydrogen Physisorption and Chemisorption
- (Q) Reproducibility of Performance

Technical Targets

Data are typically reported as surface excess gravimetric densities that reflect the amount of hydrogen sorbed due to the presence of the sorbent. Gas law

the possibility of ambient temperature operation. This optimization will require promoting narrow pore distribution in these materials, and modifications to the surface in order to increase the sorption enthalpy. An important parameter in gauging material properties that will be necessary for consideration for engineering systems is the isosteric heat, or the heat produced during the hydrogenation process. Any material system in which the isosteric heat decays with hydrogen loading, offers poor viability for engineering applications as initially high heats of adsorption result in hydrogen that is difficult to extract unless storage tanks are designed for excursions in both pressure and temperature.

Typical high surface area carbons such as activated carbons and carbon aerogels generally show great promise for use in storage tanks but the pore distributions in these materials range from microporous (<2 nm) to macroporous (>50 nm) resulting in poor volumetric densities. Framework structures also have a range of free space dimensions that can be in the mesoporous regime (2 to 50 nm) that makes a number of these materials less than ideal for storage applications. Moreover, typical sorption enthalpies of 4 to 6 kJ/mole are close to thermal energies, requiring low temperatures if large quantities of hydrogen are to be sorbed. Our work is focused on addressing both of these areas.

Recently reported work has also addressed the possibility of di-hydrogen dissociation in the presence of Group VIII catalysts, leading to the possibility that the resulting atomic hydrogen might also be a suitable means of sorbing hydrogen onto high surface area carbons. We have put considerable effort into probing the extent to which this phenomenon exists in a way that is practical to the DOE Hydrogen Program effort.

Approach

We have continued to focus our efforts over the past year in determining the behavior of unmodified carbons and the optimal microporous size distributions necessary for maximizing volumetric densities. In addition, we have considered the prospective requirements of the Engineering Center in designing a system that is capable of handling the appropriate heat transfer conduits associated with the exothermic heat of hydrogenation. Given that a concomitant goal of this project is to assess exothermic properties associated with hydrogen sorption (refueling), we continue to expend effort in determining sorption enthalpies associated with narrow pore size distributions, and in improving the fitting functions used in interpolating data points acquired from our Sieverts apparatus. We continue to perform our isosteric heat analysis through the use of an analogue of the Clausius-Clapeyron equation where $\Delta H = R[T_1 T_2 / (T_2 - T_1)] \ln(P_2 / P_1)$ [2] for isotherms taken at 77 and 87 K. We have also performed experiments at dry ice temperatures (195 K) where appropriate.

We have also re-examined work on material systems that are capable of displaying constant isosteric heat in the hopes that the physical principles behind such systems can be applied to improve sorbent design.

A large fraction of our work this past year has also been expended in spillover system synthesis and analysis. Because of the problems associated with low absolute molar quantities being measured by other research groups, we have invested heavily into producing large quantities of candidate spillover material in order to be sure that our data is free of errors associated with pressure measurements at the resolution limits of our baratron gauges.

Results

Figure 1 shows an updated version of the isosteric heat behavior of ACF10, ACF20 and a microporous CNS-201 activated carbon from Carbone Canada. The result from ACF10 is particularly important as we had believed previously that the near mono-sized pore size in this sample had a constant isosteric heat as reported last year. Subsequent analysis on our part using updated fitting algorithms shows that the isosteric heat in this sample decreases, as in all other unmodified carbons of which we are aware. In typical porous carbons, we expect the sorption enthalpy at near maximum hydrogen coverage to end up at around 5 kJ/mole. This result suggests that geometry alone will not suffice in designing an appropriate sorbent with constant enthalpy, and that some chemical modification of the surface, in addition to an appropriate slit pore geometry, will be necessary in order to maintain a constant isosteric heat.

FIGURE 1. The H_2 isosteric enthalpy of adsorption for ACF10, ACF20 and CNS201 as a function of excess adsorption. Inset: the isosteric heat is plotted as a function of the fractional amount of adsorption (excess adsorption divided by the saturation adsorption amount at 77 K).

Figure 2a shows 77 and 87 K isotherm traces from the most important of our baseline systems that we have analyzed as it is a system that demonstrates that constant isosteric heat is possible. The slit pore geometry of the Stage 2 KC24 intercalated graphite shows that some systems are indeed capable of retaining constant sorption enthalpy as a function of loading as denoted in Figure 2b, showing a nearly straight enthalpy.

Figure 3a shows how an enhanced and constant isosteric heat can perhaps obviate some of the low operating temperature concerns of physisorbents. In the case of CsC24, which has a constant 13 kJ/mole isosteric heat, nearly 2/3 of the 77 or 87 K maximum capacity of the sorbent can be achieved at 195 K as shown in Figure 3b, albeit at modest pressures of 60 bar. We believe that this is the first empirical example of a high/constant isosteric heat material that demonstrates that higher temperature sorption is possible with a high constant isosteric heat.

Figure 4 shows low and high-pressure data ranges taken from two different sample masses that were prepared for “spillover” analysis. The difficulty encountered with the measurement of small sample masses for the 1% gravimetric uptake that is typical of such systems is that the absolute molar quantities of hydrogen that are measured are at the noise limit of

FIGURE 2. (a) Shows 77 and 87 K isotherms with a blowup of the low-pressure regime in the inset. (b) Beneath the isotherms shows a plot of the isosteric enthalpy of adsorption and shows nearly constant sorption enthalpy values with loading.

typical Sieverts instruments. We have synthesized and taken measurements from roughly 0.2 and 3 gm size samples that have Pt additions and we note the extent of the error bars when the small quantities of material are measured. We have concluded from this work and other data that the overall extent of spillover is negligibly small in comparison to the absolute value of hydrogen that can be sorbed in an unmodified carbon.

Figure 5 shows a comparison of a super-activated carbon that we have analyzed for ambient temperature uptake. The sample was also measured at National Institute of Standards and Technology and that data is shown in red.

Conclusions and Future Directions

Having established the surface area dependence in carbon aerogels in previous work, we have assessed the thermodynamic effects of pore sizes in the micropore regime by probing the isosteric heat. Micropore sorbent geometries will result in higher initially isosteric heats but these values tend to drop to values that are typical of carbon surfaces as a function of loading. Our overall

FIGURE 3. (a) Shows isotherms from CsC24, a 13 kJ/mole sorption enthalpy system and shows the important 195 K isotherm, that retains a high percentage of the 77 and 87 K maximum loading value. Typical carbons would have data half of this value. (b) The lower plot shows a blow-up of the low-pressure regime.

FIGURE 4. Isotherms from spillover samples using 0.2 gm and 3.2 gm sample sizes. Our work concludes that errors in measurement and analysis from using small sample sizes can result, yielding large error bars. We have been unable to detect for the presence of the spillover effect when using large sample quantities, in any of our work.

work has seen isosteric enthalpies of adsorption at zero coverage that range from 8.5 to 5 kJ/mole. We expect these values to be typical of carbon-only-based sorbents.

Because chemical modification of carbons will be necessary to maintain a constant isosteric heat, we have looked at Stage 2 alkali metal intercalated carbons and have found that these do retain constant isosteric heat values as a function of hydrogen loading. Most importantly, in a CsC24 system, this constant isosteric heat of 13 kJ/mole results in high loading fractions over that of unmodified carbons at higher than 77 K temperatures. This system can achieve >60% of the 77 K hydrogen capacity, at 195 K.

We plan to spend the last year of this project in the synthesis and analysis of BC3 templated carbons. While the study of framework structures has been a part of our work effort over the past several years, we feel that BC3 may offer better possibilities for sorbing hydrogen given a zeolite based open structure that we intend to synthesize.

FY 2009 Publications/Presentations

1. J.J. Purewal, J.B. Keith, C.C. Ahn, B. Fultz, C.M. Brown and M. Tyagi, PRB 79, 054305 (2009).
2. Justin Purewal, Bulletin of the American Physical Society, Volume 54, Number 1 (2009).

High Pressure Adsorption Isotherms of Hydrogen on Maxsorb MSC-30 Room Temperature

FIGURE 5. Comparison of Caltech and NIST (red and black data points), with that of published values of otherwise unmodified super-activated carbon hydrogen uptake at ambient temperature as a function of pressure.

3. J.J. Purewal, H. Kabbour, J.J. Vajo, C.C. Ahn and B. Fultz, *Nanotechnology* 20, 204012 (2009).

4. "Hydrogen Spillover in Platinum Doped Superactivated Carbon." presented at the "Summer School on Methods and Applications of Neutron Spectroscopy" at the NIST Center for Neutron Research (2009).

5. "Vehicular Hydrogen Storage with Ad(b)sorbent Materials;" C. Ahn, APS Energy Research Workshop Program and Hydrogen Focus Topic Symposium chair, *American Physical Society, March 2009, Natl. Meeting, Pittsburgh.*

IV.C.1m Characterization of Hydrogen Adsorption by NMR

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Objectives

- Develop a quantitative and selective nuclear magnetic resonance (NMR) method for measuring hydrogen adsorption capacity.
- Establish molecular and atomic NMR signatures and adsorption mechanisms for adsorbed hydrogen in carbon-based and high surface area sorbent materials.
- Provide microscopic structure information on the sorbent materials and establish connection between structure and hydrogen adsorption.

Technical Barriers

This project addresses the following technical barriers from the Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (P) Lack of Understanding of Hydrogen Physisorption and Chemisorption

Technical Targets

Within the Hydrogen Sorption Center of Excellence, it is our task to use NMR to provide microscopic information on hydrogen adsorption in materials synthesized by center partners. NMR furnishes

microscopic and quantitative information on adsorption processes. It also provides information on the structure of adsorption sites. Such information provides feedback to efforts in materials synthesis and theory in designing materials to reach the DOE targets.

Accomplishments

Materials synthesized by partners were evaluated. Detailed work on doubly interpenetrated Zn-based metal-organic frameworks (MOFs), activated polyether ether ether ketone (PEEK) and carbon nanohorns of small and large diameters is based on:

- Isotherm measurements by NMR.
- NMR porosity analysis and spectral evaluation.
- Measurement of molecular dynamics.

Introduction

^1H NMR spectra allow separating contributions from gaseous and adsorbed hydrogen. NMR experiments focus on the adsorbed population and provide microscopic data as well as information on the molecular dynamics of adsorbed H_2 . Results for three samples provided by our collaborators illustrate the particular information that can be extracted from the NMR measurements. In interpenetrating MOFs the unique spectra yield evidence for a large crystal field and implicitly large binding energy experienced by the hydrogen trapped in the framework. Based on the recently developed porosimetry methodology NMR is employed to evaluate the pore structure of PEEK activated in various ways and of carbon nanohorns of different sizes.

Approach

^1H NMR efficiently detects and measures the hydrogen content of a sample and provides information on the microscopic environment and the molecular dynamics of the confined H_2 . The average pore dimensions and the exchange of hydrogen between pores can be deduced. To do so, the NMR technique is combined with a specialized setup that allows performing in situ measurements of hydrogen loading in pressures from 0.001 to 100 atm and temperatures between 77 K and room temperature.

NMR is especially useful when studying materials that show spectral distinction between free gas and hydrogen confined in micropores, as are found in

MOFs, carbon nanohorns, and activated PEEK samples. Here, combining microscopic information with isotherm measurements based on NMR line intensity measurements proves to be a powerful approach to help team members in their material design.

Results

Hydrogen Adsorption in MOFs (Collaboration with Wenbin Lin, UNC Chemistry)

MOFs are well-known for their large specific surface area and internal pore volume. However, a large internal volume can be detrimental to achieving high volumetric H_2 densities. The internal pore volume can be reduced by invoking an interpenetrating (catenating) network structure where two or more identical frameworks are assembled in parallel thereby reducing the pore volume and increasing the surface area.

We are studying the hydrogen loading of two Zn-based MOFs of nearly identical structure made up of doubly interpenetrating frameworks. The difference between them are small dangling ligands that extend into the space between the frameworks, $-OH$ and ethoxyl ($-OCH_2CH_3$), respectively. None of these MOFs will maintain a rigid crystal structure when solvent or guest molecules are removed prior to exposure to H_2 . A non-rigid framework with pliable organic linkers that move towards each other when guest molecules are removed might be advantageous for H_2 storage. When hydrogen gas is introduced into the MOF H_2 can penetrate between the organic linkers and is trapped in a strong crystal field.

NMR spectra of hydrogen loaded into double interpenetrating MOFs with $-OH$ ligands and taken at 100 K and 0.06 MPa H_2 pressure are displayed in Figure 1. The spectra show two components: a central peak associated with H_2 in voids and a characteristic double horned Pake pattern that reflects a partially averaged intramolecular dipolar interaction. The Pake powder pattern is observed when the probed hydrogen has a preferred rotational axis. This will occur when the hydrogen is exposed to a strong crystal field which will produce a concomitantly strong binding.

Spin lattice relaxation measurements taken at 87 K and 7.1 MPa yield separate relaxation times for the central peak and the Pake pattern of 33 ms and 120 ms, respectively. The result indicates that the two components of the spectra represent different populations of H_2 that do not exchange with each other, thus confirming the strong localization of H_2 molecules within the MOF framework.

It is perplexing that all hydrogen not located in large voids contribute to the Pake pattern. The recorded pattern shows a separation between the two horns of 11 kHz, down from 174 kHz for the theoretical value

FIGURE 1. 1H spectrum at 100 K and 0.06 MPa of hydrogen permeating a doubly interpenetrating MOF sample. Red trace: NMR spectrum; the double horned side peaks represent the Pake pattern while the central peak is due to gas-like H_2 in voids; blue trace: simulated Pake pattern.

obtained for the case when most hydrogen are in the lowest rotational energy state. The spectrum we observe is a temporal average of H_2 exploring various spatial sites or different energy levels over the NMR time scale. Spectra taken as a function of pressure at constant temperature and as a function of temperature at constant pressure confirm this hypothesis. The spectral width of the Pake pattern decreases with increasing pressure and temperature indicating that averaging is occurring. Further work will explore this aspect in detail.

The spectra for the second MOF that is distinguished by the ethoxyl ligands show a narrow Pake pattern, which is only observable at low temperature (100 K) and at low pressure. The narrow width of the

Pake pattern indicates that the H_2 sense a smaller crystal field. The NMR measurements strongly suggest that after removal of guest molecules, the separation between the two interpenetrating frameworks depends on the dangling ligands, with the separation being smaller and the crystal field stronger in case of the shorter $-OH$ ligands. Preliminary capacity measurements indicate a H_2 content of 6 wt% for the $-OH$ -MOF with a higher capacity for the ethoxyl-MOF.

Activation of PEEK (Collaboration with Jie Liu, Duke)

In order to achieve high gravimetric as well as volumetric hydrogen capacities for materials that rely solely on sorption mechanism the pore volume has to be maximized while keeping the pore diameter in the micropore range ($d < 2$ nm). Surface area is the determining parameter and pores with diameters $d \leq 1$ nm will exclusively accommodate adsorbed H_2 while pores with larger diameter provide space for gaseous H_2 as well, reducing the volumetric H_2 density.

PEEK, a high performance polymer, was selected to maximize micropore volume through activation. The material was carbonized at 900°C in Ar ambient and subsequently activated in either CO_2 or steam at 900°C for various time durations. The resulting porous material was characterized by the burn-off, defined as the relative weight loss during activation. Steam activation required longer activation time for equivalent burn-off and was considered the “milder” method.

NMR porosimetry developed over the last year is able to distinguish between materials incorporating only narrow pores and materials with pores that are larger than 1 nm. In short, hydrogen in pores with diameters smaller than 1 nm will produce an NMR line that does not change position with increasing H_2 pressure. Conversely, larger pores which contain two populations of hydrogen – adsorbed and gaseous – will generate NMR lines that move with increasing H_2 pressure. The rate at which a line moves with pressure increases with the increasing pore diameter.

Figure 2 shows the variation of the line position for confined H_2 for PEEK samples with various amounts of burn-off. Within error, CO_2 activation with 1 and 20% burn-offs and steam activation creating burn-offs of 20 and 35% produce homogeneous microporous material as evidenced by an NMR line that does not shift with pressure. Activation producing severe burn-off creates a heterogeneous pore distribution, containing micro and mesopores, shown clearly by the NMR line position that varies with H_2 pressure. The rate at which the line position changes as function of H_2 pressure increases with increasing burn-off indicating that the pores are getting progressively wider and more volume for a gaseous population is created. Indeed, a

FIGURE 2. ^1H NMR line shift observed at 100 K as a function of H_2 pressure for H_2 in pores of PEEK activated via CO_2 (filled symbols) and steam (open symbols) to achieve various degrees of burn-off: ■ : 1 %; ▲ : 26 %; ● : 59 %; ◆ : 80 %; □ : 20 %; ▽ : 35 %; △ : 47 %; ○ : 70 %; ◇ : 95 %.

linear correlation is observed when the line position at constant pressure is plotted versus burn-off for all samples, regardless of activation method, again indicating that burn-off beyond 20% for CO_2 and 35% for steam will primarily create mesopores. CO_2 activation with 59% burn-off and steam activation yielding 70% burn-off produce very similar NMR shift values as a function of pressure indicating that although the steam produced higher burn-off the pore distribution is similar. In this direct comparison steam appears to be a “milder” activation method producing a higher percentage of narrow pores than when CO_2 was used as a medium.

It is intriguing that the observed shift for all samples at low pressure (or when extrapolated to low pressure) attains the same value, indicating that in all samples the adsorbed hydrogen senses the same chemical environment. Therefore, the chemical nature of the surface is independent of the amount of burn-off.

The total hydrogen population of pores increases linearly up to 60% burn-off (CO_2) and then appears to decline. This trend indicates that beyond 60% burn-off surface area is lost by mesopores merging into larger mesopores and macropores.

Small and Large Carbon Nanohorns (Collaboration: David Geohegan, Oak Ridge National Laboratory)

The Oak Ridge group has succeeded in synthesizing carbon nanohorns (CNH) with either small or large

diameters. Samples are either pristine or subjected to a mild oxidation procedure. When oxidized the walls of the CNHs are compromised and H_2 can access endohedral as well as interstitial pores. Conversely, in pristine samples only interstitial spaces are accessible. NMR evaluated how these different volumes and their accessibility contribute to hydrogen storage. To do so, a combination of spectral analysis and porosimetry (see PEEK) were employed.

Previous measurements showed that small pristine CNHs have no capacity for H_2 storage while small, opened CNHs show H_2 storage in narrow pores. We concluded that interstitial sites in small pristine CNHs are not accessible to H_2 indicating that the interstitial sites have on average diameters smaller than 0.3 nm. The mild oxidation treatment, however, succeeded in opening holes in the walls of the nanohorns making the endohedral spaces accessible to H_2 . Because the NMR line did not shift with applied H_2 pressure, the endohedral pores have diameters $d \leq 1$ nm.

Figure 3 shows 100 K spectra of hydrogen permeating samples of large CNHs with the pristine sample displayed on top and the oxidized sample on the bottom. Hydrogen in the pristine sample produces a well defined line at -11 ppm that does not shift with H_2 pressure. Therefore, H_2 adsorbs in interstitial pores that in this sample composed of large CNHs are adequate to accommodate H_2 but also sufficiently narrow to provide space for adsorbed H_2 only.

When compared with the pristine sample, the NMR line associated with confined H_2 shifts upfield (to the right in Figure 3 bottom) in the oxidized sample. In addition, a new line emerges with increasing pressure at approximately -35 ppm. Since oxidation creates holes in the walls of CNHs H_2 can exchange between the interstitial and endohedral volumes. One exchange narrowed line will be observed with a shift intermediate between those for H_2 in interstitial and endohedral spaces. Interstitial H_2 displays a shift of -11 ppm and if endohedral H_2 is associated with the emerging line at -35 ppm then the exchange line will be intermediate to those limiting values. With increasing pressure the observed line will move towards the lower shift values (to the right) as the interstitial spaces are filled and more H_2 will accumulate in the endohedral volume. This trend is observed.

NMR shows conclusively that in large open CNHs H_2 will fill interstitial and endohedral sites and will exchange between the interconnected spaces. The interstitial pores are preferred adsorption sites that are occupied first presumably because the pore diameters are narrower than in the endohedral spaces.

FIGURE 3. 1H spectra at 100 K of H_2 permeating large carbon nanohorn samples as function of H_2 pressure. Top: pristine sample; bottom: oxidized sample (the void or free gas peak is dominant in the spectra at the bottom because the sample filled only part of the NMR coil volume).

Conclusions and Future Directions

- Hydrogen in MOFs experience unexpectedly large crystal fields promoting strong binding and high H_2 capacity.
- It was unpredicted that the non-rigidity of the doubly interpenetrating MOF framework under removal of guest species would promote efficient trapping of H_2 .
- Subtle differences in MOF design, in particular the length of the employed ligands dangling between the two interpenetrating frameworks lead to observable

- differences in H₂ adsorption and require further study.
- Spectra will be obtained as a function of temperature down to 4 K to elucidate the nature of the hydrogen producing the Pake pattern. Relaxation measurements will complement that study.
 - Activation of PEEK leads to microporous material for burn off values below 35% when steam activation was used.
 - The total H₂ capacity of pores obtains a maximal value for materials with burn off at 60%.
 - The nature of the adsorbing surface remains unchanged even for material with the highest burn off value.
 - Opened large carbon nanohorns confine H₂ in an interconnected space composed of interstitial and endohedral sites.
 - Adsorption occurs predominantly in the interstitial volume at low pressure with the endohedral volume being filled with increasing pressure.
 - H₂ adsorption of boron substituted material has been a major focus of the NMR work and will be continued. Direct evidence of the boron-hydrogen interaction will be provided through double resonance experiments.

- Microscopic structure information is being obtained on new boron substituted material of high boron content (National Renewable Energy Laboratory).
- Work on hydrogen adsorption in porous polymers (Argonne) is being continued.

FY 2009 Publications/Presentations

1. Enhanced binding energy and slow kinetics of H₂ in boron-doped graphitic carbon, Alfred Kleinhammes, Robert J. Anderson, Q. Chen, Youmi Jeong, T.C. Mike Chung, and Yue Wu, submitted to Phys. Rev. Lett. (under review).
2. Synthesis of Micro-porous Boron-Substituted Carbon (B/C) Materials using Polymeric Precursors for Hydrogen Physisorption, T.C. Mike Chung, Youmi Jeong, Alfred Kleinhammes, and Yue Wu, ECS Transactions (submitted).
3. Unexpected quantum effects observed by NMR for adsorbed hydrogen in interpenetrating MOFs at high temperature, Alfred Kleinhammes, B.J. Anderson, Wenbin Lin, Liquing Ma, and Yue Wu, Fall MRS Meeting (submitted Talk).

IV.C.1n Advanced Boron and Metal-Loaded High Porosity Carbons

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- (A) System Weight and volume
- (B) System Cost
- (C) Efficiency
- (D) Durability/Operability
- (E) Charging/Discharge Rates
- (P) Lack of Understanding of Hydrogen Physisorption and Chemisorption
- (Q) Reproducibility of Performance

Technical Targets

This project conducts fundamental studies of the hydrogen-substrate interaction to develop novel classes of electron-deficient framework materials based on carbon and boro-carbon aromatic networks, including a subclass wherein light metal atoms are dispersed on the framework to both facilitate spillover effects and to directly adsorb hydrogen. We have recently demonstrated substantial enhancement in the interaction of hydrogen with such a modified surface, increasing the adsorption energy from the 4–6 kJ/mol typical of standard carbons and silica aerogels to 12.5–15 kJ/mol, near the target adsorption energy of 15–30 kJ/mol. In the previous year, we have built upon our demonstration that boron incorporation facilitates uptake of nano-dispersed metals, obtaining detailed information on the local bonding geometry (a requirement for further optimization) and extending this result to the Ti system (with a large number of empty d orbitals potentially suitable for interaction with H₂). We have further developed a testbed for investigating spillover effects by in situ measurement of transport and optical signatures of stored hydrogen in a well-characterized nanoscale geometry, developing suspended membrane devices with integrated transport leads and characterizing these devices' response to adsorbed species. A novel boron-nitrogen (BN) framework system that is resistant to formation of bulk BN upon hydrogen removal (and hence may afford improved reversibility) has been simulated. We are continuing towards the goal of developing sorbents which can meet the DOE 2015 hydrogen storage targets for gravimetric and volumetric storage densities at reasonable cost in a reversible system, although further breakthroughs in synthesis will be necessary to simultaneously increase boron content, tune local geometries, increase porosity, exploit spillover, control chemical frustration, and obtain optimal local hydrogen binding properties throughout the macroscopic sample.

Objectives

- Identify new materials system with high surface area in boro-carbons and metal-boro-carbons with surface chemistry tuned for a stronger hydrogen binding interaction that will enable 2015 DOE-target volumetric and gravimetric reversible hydrogen storage capacity, through a combination of materials synthesis, characterization and first-principles computation.
- Synthesize highly porous boro-carbons and metal boro-carbons with simultaneous ultra-high boron content, high surface area, tuned and optimized pore distributions, controlled spillover effects, metal loading, and tunable curvature.
- Enhance the stability of highly dispersed metals on boro-carbon frameworks, including atomic-level dispersion that is stable against aggregation, by tuning electron deficiency.
- Maintain these properties in a system with moderate economic cost of raw materials and stability over many cycles.

Technical Barriers

This project addresses the following technical barriers from the x section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

Accomplishments

- The binding energy for H_2 as measured by isosteric heats of adsorption has been increased to ~ 15 kJ/mol, much higher than in conventional activated carbons (4–6 kJ/mol), due to the presence of boron. These values approach those necessary for high-capacity reversible room-temperature hydrogen storage (15–30 kJ/mol). The next task is to maintain these high values through a greater surface area. Deposition of BC_3 onto aerogel frameworks and optimization of B-containing precursors and LiCl pore-formers are being pursued towards this goal.
- Demonstrated that incorporation of boron into nanoporous carbon framework improves the uptake of nanodispersed metals Pt, Zr and now also Ti, in accord with goals in atomic dispersion of metals for enhanced wt% and volumetric hydrogen storage, following computational predictions for hydrogen binding energies of 30 kJ/mol in light-weight frameworks designed to be resistant to aggregation. These systems also demonstrate spillover.
- A BC_{12} material with specific surface area (SSA) = $780\text{ m}^2/\text{g}$ shows H_2 binding energy 20–10 kJ/mol and more than doubles H_2 absorption capacity per surface area compared to prior materials. A BC_8 material with SSA = $330\text{ m}^2/\text{g}$ shows even higher H_2 adsorption capacity per surface area (3.8 wt% at 77 K). A BC_6 material with 15% B has been prepared, but with very low SSA. Transition metal doped BC_x materials exhibit well-dispersed Pt, Ti, Zr nano-particles (size $< 2\text{ nm}$).
- Novel adsorptive strategies involving framework stabilization of BN systems are being pursued computationally in exploratory work aimed at opening up a novel materials strategy for enhanced hydrogen storage.

Introduction

Before our investigations, only a few reports discussed the activated carbon with acidic boron groups, in dense morphologies with crystalline structure and limited compositions: either very low boron content ($< 2.35\text{ mol}\%$) from B doping of graphitic C at high temperature or very high boron content (25 mol%) in BC_3 from chemical vapor deposition reaction of BCl_3 and benzene. A new class of hydrogen sorbents with enhanced hydrogen binding energies in a low-mass framework shows potential to meet DOE gravimetric targets, with further optimization. The introduction of boron into a curved high-surface-area carbon framework induces electron deficiency and so increases the propensity to bind H_2 reversibly at energies intermediate between traditional physical and chemical adsorption.

Additionally, we have demonstrated through first-principles calculations that this same electron deficiency can help stabilize the atomic dispersion of light metal atoms. The exposed orbitals of these atoms then provide another venue for new binding chemistry in a geometry that is naturally resistant to aggregation due to the rigidity of the porous framework. We also continue to develop improved means to control porosity and activate surface area in heavily boron-doped carbons, expanding the number of dispersed metals, and new candidate materials with novel nanometer-scale chemistry to be exploited for hydrogen storage.

Approach

Our approach intimately couples the synthetic, computational and characterization efforts locally at Penn State with the world-leading characterization tools (and also synthetic and computational efforts) available throughout the Center to break new ground in the discovery of new materials systems that modify the binding chemistry towards hydrogen at a fundamental level by controlling electron content, local bonding geometry and spillover geometry in a rigid framework. The starting point, a boro-carbon-based nanoporous framework, provides a robust, lightweight, high surface area, mechanically rigid, low-cost system with the structural cohesiveness to withstand the substantial variations in local chemistry that are necessary to induce enhanced hydrogen adsorption. These modifications include withdrawing substantial numbers of electrons from the structure, dispersing exposed metal atoms onto the structure, and forcing topologically or topographically frustrated geometries that have the potential to generate large local electric fields, resistance against aggregation, and open-shell electronic configurations. Pyrolysis of carefully designed boron-containing polymeric precursors, which are the polyaddition adducts of phenylene diacetylene (with and without lithiation, see Figure 1) and BCl_3 , has shown significantly higher hydrogen binding energy and physisorption capacity, compared with the corresponding carbonaceous materials. Each of these final states: electron deficiency, exposed uncompensated orbitals, and uncompensated local fields, provides a distinct fundamental means to generate new classes of adsorptive interaction that is intermediate between traditional chemical and physical adsorption and in the optimal range for reversible room-temperature hydrogen storage. In all stages of this process careful attention is paid to DOE goals in materials cost, volumetric and gravimetric density, and stability over multiple cycles.

Results

The research team has extended studies to include an additional synthetic method (BC_3 deposition onto highly porous aerogels), additional metals (e.g. Ti),

FIGURE 1. Top: Synthesis route for preparing porous BC_x and $Pt_aB_bC_c$ materials. Bottom: ^{11}B magic angle spinning nuclear magnetic resonance (NMR) spectra of BC_x samples prepared from pyrolysis of precursor (I) at 150: a, 600: b, 800: c, and 1,100: d °C. The lower of two peaks corresponds to the desired aromatic boron – its upshift after heat treatment indicates a desirable greater electron deficiency. Excessive heat treatment leads to a crystalline non-porous material. $LiCl$ pore formers ameliorate this effect.

spillover testbeds, and simulations of new framework materials. For enhanced H_2 physisorption it is important to simultaneously optimize several materials properties: micro-porous B/C material (Figure 2) with both a high surface area and a substantial electron deficiency, stabilizing dispersed metals whose open orbitals then provide sites for enhanced hydrogen binding and spillover.

X-ray investigations of the structure of $LiCl$ in the previous year provide greater control over these important pore-forming agents. At pyrolysis below 400°C, $LiCl$ shows no diffraction peak. Above 400°C, sharp diffraction peaks reflect the presence of hydrated and anhydrous $LiCl$ crystals. These in situ formed $LiCl$ molecules in the boron precursor are conveniently used as pore-forming additives removable by water-washing. A shift from micropores when treating at 600°C to predominately mesopores at 800°C is consistent with $LiCl$ agglomeration above its melting temperature. The combination of additives and pyrolysis temperature

FIGURE 2. Top: Scanning electron micrograph of BC_x obtained after pyrolysis at 600°C, maintaining porous structure in a highly boron-doped carbon. Bottom: Transmission electron micrograph of a $Ti_aB_bC_c$ with dispersed Ti particles (actually TiO_2 , due to oxygen exposure) containing 12 wt% Ti and 6.9 wt% B.

offers a tool to control B_bC_c morphology. External additives such as $NaBH_4$ enhance boron content and porosity in the final products. Other porosity-enhancing additives with higher melting temperatures and good solubility for removal from BC_x matrix have also been developed in the past year. Several porous BC_x materials show consistent B content up to 15%. Results for samples 5 and 7 are given in Figure 3. These samples maintain high adsorption energy to high surface coverage, significantly higher than those observed in undoped carbons (4 kJ/mole) and some metal-doped C materials. The increase of B content increases the hydrogen binding energy, as shown in the figure.

Introduction of metal nanoparticles plays an important role in hydrogen adsorption and binding energy. H_2PtCl_6 was deposited from aqueous solution and platinum acetylacetonate was reduced to platinum nanoparticles using ethanol and ultraviolet radiation on the surface of high surface area nanoporous carbon derived from perfluoroalkoxy with a mean pore size of ~0.8 nm. These investigations were

FIGURE 3. Top: Comparison of hydrogen adsorption for BC₆ (sample 7) and BC₁₂ (sample 5) at 77 K. Although sample 5 has a lower specific surface area, it has a larger uptake due to a stronger H₂ binding from the higher B content. Bottom: Comparison of hydrogen adsorption for BC₁₂ containing 1 wt% Pt and the corresponding pure BC₁₂ at 293 K. Pt increases the hydrogen uptake, possibly from spillover. The hydrogen binding energy is at the edge of the range needed to hit DOE 2010 targets, but the specific surface area, boron content, and metal loading must be optimized to obtain this binding energy over more sites.

extended to Ti metal. Figure 2 shows a transmission electron micrograph of a Ti_aB_bC_c material containing 12 wt% Ti and 6.9 wt% B, which was prepared by bis(cyclopentadienyl)titanium dichloride in toluene solution, then following the same thermal reduction. Due to the air-sensitivity of Ti, the observed nanoparticles are TiO₂. The resulting M_aB_bC_c material maintains a porous structure with slightly reduced surface area. Figure 3 compares hydrogen adsorption at 273 K for a pair of BC_x and Pt_aB_bC_c materials, in which Pt_aB_bC_c was prepared from BC₁₂ containing only 1 wt% Pt nanoparticles. The remarked increase of hydrogen adsorption, from 0.38 wt% to 0.6 wt%, is associated with Pt nanoparticles (1–2 nm) in intimate contact with BC_x, possibly as H₂ spill-over. Pt_aB_bC_c reversibly physisorbs hydrogen at ambient temperature under moderate H₂ pressure (<90 bar). Absorption isotherms indicate an H₂ binding energy of greater than 15 kJ/mol.

In an alternative synthetic technique, boron trichloride and benzene (2:1 by volume) were mixed in a He carrier gas and deposited on a high surface area mesoporous silica aerogel in a 900°C tube furnace. The deposited BC₃ was then analyzed using X-ray photoelectron spectroscopy and ¹¹B NMR spectroscopy. After BC₃ deposition, the surface area reduced slightly from 730 m²/g (heat-treated aerogel alone) to 670 m²/g. Heat of adsorption using adsorption isotherms at 77 and 87 K indicates that the BC₃ coating dramatically increases the initial heat of adsorption, from ~4 kJ/mol to ~9 kJ/mol, with a nearly double heat of adsorption maintained at higher hydrogen loadings onto heterogeneous sites (Figure 5). The H₂ uptake at 77 K increased from 50 cc/g to 80 cc/g, even though the surface area decreased. This new method of creating highly porous boro-carbons enables further independent tuning of porosity and boron content, up to 25% boron.

A testbed to elucidate the critical mechanism of spillover, a single-graphene-layer device with simultaneous transport and Raman probes, has been further developed. We have previously dispersed uniform Pt nanoparticles onto the graphene sheet, and we have recently produced the requisite graphene-based field effect transistors and characterized them under controlled gas environments, including suspended graphene field effect transistors that use buffer-oxide etching to remove the substrate, as shown schematically in Figure 4. The position of the Dirac peak (resistivity maximum) with respect to the gate voltage reveals the charge transfer from the adsorbate to the high surface area substrate – this transfer is a critical mechanism in enhancing hydrogen adsorption. Characterization with aromatic adsorbates, depicted in the figure, demonstrate the feasibility of the approach. An additional device containing Pt nanoparticles was also prepared and is currently under study, with electric measurements under controlled pressure and gas flow.

Calculations of the relative stability of various ordered and disordered high surface area boro-carbon and metal boro-carbon systems continue to support the experimental efforts. In addition, possible new materials systems continue to be investigated. For example, stabilization of atomically dispersed metals through topological frustration with halogen electron acceptors appears fruitful, and a new framework system that exploits weak hydrogen binding to boron-nitrogen motifs in a geometry that suppresses the formation of BN is also showing preliminary promise as a new strategy towards the challenge of hydrogen storage, as depicted in Figure 6.

Conclusions and Future Directions

Our synthesis approaches to produce high surface area materials with high boron content demonstrated

FIGURE 4. Top: Schematic of a suspended graphene field effect transistor testbed for spillover investigation. Bottom: Charge transfer to the substrate reflects shifts in the gate response in terms of the number of adsorbate π electrons: the device is sensitive to electron deficiency.

FIGURE 5. Heat of adsorption vs. H_2 loading for silica aerogel and BC_3 coated aerogel. Although the coated material has a slightly lower specific surface area, it demonstrates improved hydrogen adsorption due to a near-doubling of the binding energy for H_2 .

that boron substitution into the sp^2 lattice produces an increased binding energy for H_2 , one that is further enhanced by highly dispersed metals. We continue

FIGURE 6. Left: A new material system being assessed via first-principles simulation: an open covalent BN framework adsorbs H in a manner that suppresses formation of solid BN, hence improving reversibility. Right: A halogen dimer constraints to the underside of the boro-carbon sheet enhances the stability of an isolated Ti atom on the other side, thereby solving the primary challenge of dispersed exposed metallic atoms: suppressing aggregation.

to increase the boron content, porosity, and hydrogen binding, with computational guidance on optimizing surface chemistry via induction of high curvature, electron deficiency, large local fields, and exposed metal orbitals that are resistant to aggregation. The choices of metals to disperse is guided computationally via modeling of the interaction with B. These efforts are focused on obtaining very large densities of homogeneously distributed binding sites of 15–30 kJ/mol binding in a lightweight framework, which will provide a possible pathway to DOE 2015 targets for gravimetric and volumetric storage. Work to date has led to ~150% improvement in binding energy (nearly to the goal), validating the underlying design concept for these new advanced sorbents. The team will focus these efforts on further reducing the particle sizes of an expanding range of metals by optimizing loading conditions and thermal budgets, and pursuing multiple parallel strategies to optimize porosity while maintaining optimal local bonding geometries and boron contents. The effect of increased binding energy on high surface area nanoporous borocarbons on processes such as hydrogen spillover from noble metals like Pt will be examined in detail with new testbed geometries.

FY 2009 Publications/Presentations

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2. Transparent Boron-Doped Carbon Nanotube Films, X.M. Liu, H.E. Romero, H.R. Gutierrez, K. Adu, P.C. Eklund, Nano Letters **8**, 2613 (2008).
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8. *A simple approach to synthesize nanoporous carbons with high heats of adsorption of hydrogen*, R. Rajagopalan and H. Foley, submitted to JACS.

IV.C.1o NIST Center for Neutron Research in Support of the Hydrogen Sorption Center of Excellence (HSCoE)

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Project End Date: Project continuation and
direction determined annually by DOE

Objectives

- Quantify the amount, location, bonding states and dynamics of hydrogen in hydrogen sorption materials.
- Direct partner synthesis efforts based on the understanding gained through the use of scattering techniques.
- Demonstrate the fundamental characteristics of useful hydrogen storage materials.

Technical Barriers

This project addresses the following technical barriers from the Storage section (3.3) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (P) Lack of Understanding of Hydrogen Physisorption and Chemisorption

Technical Targets

NIST provides important materials metrologies for Center partners using neutron-scattering measurements to understand and characterize hydrogen-substrate interactions of interest to the Center.

Enhanced Hydrogen Storage using Supported Metal Centers

This project is conducting fundamental studies of how hydrogen binds in metal-organic frameworks (MOFs) with exposed metal sites. Insights gained from these studies will be used by Center partners and applied toward the design and synthesis of hydrogen storage materials that meet the following DOE hydrogen storage targets:

- Cost: \$4/kWh net
- Specific energy: 1.8 kWh/kg
- Energy density: 1.3 kWh/L

Accomplishments

- Determined bulk elemental compositions of materials of interest to the Center. These include metal-decorated carbon-based materials, MOFs, and Boron-infused carbon materials. This understanding helps to speed sample development and material synthesis aimed at reaching the DOE goals of specific energy (1.8 kWh/kg) and energy density (1.3 kWh/L).
- Determined the location of hydrogen binding in several crystalline materials. Provides atomistic understanding of how hydrogen is adsorbed and confirms newly developed theories.
- Illustrated the site-specific hydrogen adsorption strength in MOF materials. The overall appreciation of this determines the isosteric heats of hydrogen adsorption. The size and shape of the Coulomb potential determines inelastic neutron scattering features. Spectra are composed of rotations and multiple rotation-phonon transitions.
- Confirmed that spillover is small for a particular Pt-single-wall nanohorn (SWNH) sample using multiple techniques.

Introduction

To obtain the DOE levels of hydrogen storage in a timely manner, it is imperative that trial-and-error testing of materials be avoided. Thus, the focus must be upon the rational design of new systems. From a thorough understanding of the physics and chemistry that governs the hydrogen-substrate interactions, we will be able to make a more concerted effort to push the frontiers of new materials. The key to improving materials is a

detailed understanding of the atomic-scale locations of the hydrogen and determining how it gets there and how it gets out. Neutron scattering is perhaps the premier technique for studying hydrogen and the NIST Center for Neutron Research is currently the leading facility in the U.S. for studying these materials.

Approach

NIST provides important materials characterization for Center partners using neutron-scattering measurements to probe the amount, location, bonding states, dynamics, and morphological aspects of hydrogen in carbon-based materials such as polymers, MOFs, and carbonaceous materials such as carbon nanohorns. NIST works directly with Center partners that produce novel hydrogen storage materials to analyze the most promising samples and to help determine and resolve the fundamental issues that need to be addressed.

Results

Enhanced Physisorption

NIST and the National Renewable Energy Laboratory (NREL) co-lead this development effort within the HSCoE focused on understanding interactions with metal ions and focuses on the rational synthesis of sorbents that can strongly bind multiple di-hydrogen ligands. Di-hydrogen ligands may be bound to a single metal atom with binding energies in a desirable range for vehicular hydrogen storage. The synthesis of materials that have open, isolated metal sites exhibiting moderate H_2 binding energies, with interactions potentially similar to those observed in Kubas-type complexes, are explored and optimized by the appropriate Cluster members. Key issues are balancing the reactivity of the hydrogen sorption sites with their stability and hydrogen capacity given a 2 bar delivery pressure.

MOFs exhibiting stronger binding interactions are needed to facilitate H_2 adsorption at higher temperatures, and, indeed, a binding energy of 15-20 kJ/mol has been predicted to maximize the amount of adsorbed H_2 accessible at 298 K and up to 20 bar [1]. We have previously used neutron powder diffraction to demonstrate that the highest (at the time) observed maximum isosteric heat of adsorption (10.1 kJ/mol) observed for a MOF was directly related to H_2 binding at coordinatively unsaturated Mn^{2+} centers within a framework [2]. This observation also held for other MOFs with coordinatively unsaturated metal centers (CUMC) of different metal ions [3-5] and also speculation of the Kubas binding nature of the hydrogen [6].

The first evidence for CUMC- H_2 interactions [7] came from low-temperature infrared spectra of a

nanostructured MOF, HKUST-1 [8]. This revealed at least three distinct binding sites with induced red-shifts in the vibrational mode frequencies attributed to site-specific binding energies ranging from (2.5 to 4) kJ mol⁻¹ with the molecule undergoing relatively free rotation. Powder neutron diffraction experiments located the hydrogen adsorption sites and conclusively verified that initially D_2 binds to the unsaturated coordination sites of the Cu^{2+} -carboxylate paddle-wheel building units [9], followed by filling of the small cages before the Cu^{2+} site is fully saturated [9,10]. Filling of the larger pores followed along with some structural rearrangement of the dihydrogen molecules in the smaller pore. The distance between the metal and the centroid of nuclear deuterium scattering is 2.39(1) Å, a much-reduced distance from that typical of van der Waals interactions. This interaction should also be compared to the range of M-H distances from ca. 1.7 to 1.9 Å found in the well-known organometallic ‘Kubas’ compounds where there is evidence for electron donation from the dihydrogen to transition metal and elongation of the H-H bond through back bonding [11].

To address this issue further, we used inelastic neutron scattering (INS) and first-principles computer simulations to gain additional insight into the framework structure of HKUST-1 and to provide a detailed understanding of the local potential of para-hydrogen ($p-H_2$) adsorbed at the primary metal adsorption site (Figure 1). The form-factors of the three main rotational peaks follow that expected for a free hydrogen molecule with a regular H-H intra-molecular bond distance and provide evidence against a Kubas-type interaction. The form-factors associated with the individual adsorption sites are characterized by differing Debye-Waller factors reflecting the strength of the site-specific adsorption strengths. Based on our calculated potentials using the density functional theory formalism and generalized gradient approximation (GGA) functional, we can assign all the features observed in the INS data for hydrogen adsorbed in HKUST-1 (Table 1). We find that the orientational potential is slightly two-dimensional and dominated by a small Coulombic term, hence there is a tendency for the H_2 to lie in a plane perpendicular to the Cu-Cu bond. The in-plane rotation is almost free and unhindered. The features observed at 9.1, 12.75 and 14.0 meV with increasing H_2 loading are due to rotational transitions from $J = 0$ to 1, $M = \pm 1$. The other features observed in the data are due to rotation-rotation or rotation-phonon excitations.

Engineered Nanospace

Although the crystal structures of MOFs are typically composed of rigid frameworks, they can demonstrate significant structural distortions upon adsorption/desorption of guest molecules. An extreme aspect of this type of distortion occurs as a “breathing”

FIGURE 1. (Upper) Difference inelastic neutron scattering spectra of *p*-H₂ loaded HKUST-1 and the bare substrate measured on FANS. The displayed spectra result from *p*-H₂ scattering only and peaks of significant intensity are labeled as either rotations (Rot) or combination rotation and transition (Trans). Ratios of *p*-H₂ to copper are 0.26 (blue circles, adsorption at Cu site only) and 1.1 (green circles, adsorption at Cu site and 2nd site). (Lower) The orientational potential of H₂ located at the (x,x,0) adsorption site in HKUST-1. Top-left panel shows the primitive lattice vectors (a,b,c) and the local coordinate system (x',y',z') which was taken to describe the H₂-orientation. Top-right panel shows the contour-plot of the potential mapped on a sphere representing the H₂-orientation θ - ϕ . The potential maximum is at $\theta = 0^\circ$ (H₂ parallel to z-axis) (z'-pole (red), zero of energy) and the potential minimum is at the $\theta = 90^\circ$ (x'-y' plane (blue), -78 meV). The left-bottom panel shows how the potential changes as the H₂-molecule is rotated around Cu-Cu axis. The right-bottom panel shows the variation of the potential with θ for fixed $\phi = 0$.

effect that is typically associated with a large change of the internal pore volume. Last year's report detailed our initial results on the MIL-53 system (collaboration with General Motors Corporation) aimed at evaluating

TABLE 1. Orientational potential obtained from GGA calculations and the corresponding rotational levels. The calculated classical harmonic H₂ phonons for a fixed H₂ orientation perpendicular to the Cu-Cu bond are $\omega(x') = 9.56$ meV, $\omega(y') = 13.44$ meV and $\omega(z') = 22.87$ meV. The coupling of phonons with rotational transitions explains the observed INS spectra.

H₂ rotational levels for an orientational potential: $V(\Omega) = V_0 + \sum_{lm} A_{lm} Y_{lm}(\Omega)$ $V_0 = -53.3$ meV, $A_{20} = 82.0$ meV, $A_{22} = 0.2$ meV, $A_{40} = 3.0$ meV, $A_{60} = 1.0$ meV			
State #	Energy (meV)	$E_i - E_0$ (meV)	Major JM
0	-61.47	0	J=0, M=0
1	-51.85	9.61	J=1, M=+/-1
2	-51.71	9.76	J=1, M=+/-1
3	-25.39	36.08	J=2, M=+/-2
4	-25.39	36.08	J=2, M=+/-2
5	-24.20	37.27	J=1, M=0

the applicability of this mechanism to achieving the hydrogen storage goals associated with developing high specific surface area materials with optimized pore geometries.

The coarsely defined hysteresis of MIL-53(Al) observed under varying temperature [12] was better defined using synchrotron X-ray radiation. We further undertook several neutron studies aimed at describing the adsorbed hydrogen structures not only at low temperatures (4 K), but also through a complete hydrogen adsorption/desorption isotherm at 77 K. At low loading the hydrogen resides in the residual open-pored phase and gradually forces open the closed-pores upon further adsorption with multiple adsorption sites being occupied to saturation. Upon desorption, there comes a situation where there is no residual pressure in the system, but the framework traps ≈ 1 wt% of the hydrogen in the closed-pores. The H₂ remains in closed pore even when pumping under high vacuum to well over 100 K (Figure 2).

Substituted Materials

NIST has contributed to the efforts of developing materials with high concentrations of substituted atoms (e.g., B on graphene structures) using non-destructive bulk elemental determination from prompt-gamma activation analysis (PGAA) of Center synthesized samples. The results of the PGAA analysis has been successful in steering synthetic approaches of the Center members interested in optimizing the dopant contents of micro- and nano-porous carbons. Continued efforts in small-angle neutron scattering and INS measurements on nano-porous carbons have been used to gain insights into the morphology of the pore structure and how hydrogen is adsorbed into these materials with several Center members (Blackburn, NREL; Ahn, Caltech;

FIGURE 2. Sequential adsorption of D_2 in MIL-53 at 77 K. D_2 (0.5 bar) initially occupies the un-transformed open-pore crystal phase and gradually forces open the majority closed-pore phase (2 bar). The D_2 adsorption sites are saturated at ≈ 4 bar D_2 pressure after which we reduce the pressure also whilst monitoring the neutron powder diffraction patterns. The natural tendency for the framework to ‘close’ at 77 K results in some trapping of the hydrogen that is then difficult to remove without extensive heating and application of high-vacuum.

Pfeiffer, University of Missouri). Detailed INS of the hydrogen rotational spectra in BC_8 materials prepared by NREL showed similar characteristics compared to a similarly prepared carbon material though the hydrogen is more apparently rotationally hindered through the entire adsorption range in BC_8 than for the pure carbon. However, desorption studies with temperature, indicate that both materials retain similar amount of hydrogen between 60 K and 85 K.

Spillover Materials

NIST has continued efforts to identify the final state of spillover hydrogen in several Center produced materials, though clear results have been elusive. Parallel efforts to use gas adsorption apparatus to produce a one shot determination of spillover amounts have been successful, with the observation of ≈ 0.08 wt% hydrogen spillover in a Pt-SWNH (Oak Ridge National Laboratory) sample, that corresponds well to the 0.17 wt% determined from INS on the same sample (previously measured by us). Additionally, we have working with collaborators from Monash University (Australia) to attempt to observe the spillover and general hydrogen dynamics in zeolites-templated microporous carbons. Despite several attempts at synthesis and platinum incorporation, the isosteric heat of adsorption for hydrogen remains around 7 kJ/mol with no additional indicators from spillover apparent. Apparently, the pore structures in the templated carbon are such that the INS of the hydrogen spectra are broad and liquid-like and there seems to be two types of hydrogen diffusing on two different timescales at 77 K as determined by quasi-elastic neutron scattering. Further work is needed to fully understand these developments.

Conclusions and Future Directions

The main conclusions of this years work can be summarized as follows:

- Determined that open metal centers in MOF materials do not exhibit to any H-H bond elongation upon adsorption and hence are not Kubas-type complexes.
- Determined the temperature dependence of the structural transition in a flexible framework material, MIL-53 with precision.
- Determined the structural dependence of MIL-53 throughout the isotherm cycle and that the natural tendency for the framework to close at 77 K causes some trapping of ≈ 1 wt% hydrogen.
- Determined characteristic rotational spectra with adsorption for several nano-porous substituted and pure carbon materials.
- Zeolite-templated carbons exhibit liquid like hydrogen recoil, even at low coverage, and there are two timescales for hydrogen diffusion at 77 K.

Currently, only a few MOFs exhibit the capacity to adsorb multiple H_2 per metal center. We will look at the most promising materials that could exhibit this behavior to determine the viability of this approach given the non Kubas-type adsorption we have observed. We will continue to aid the other Center partners in characterizing their materials aiming to understand the fundamental characteristics that improve hydrogen storage capabilities.

Special Recognitions & Awards/Patents Issued

1. Jae-Hyuk Her: winner of the 2009 Sigma-Xi NIST Chapter Postdoctoral Poster Prize.

FY 2009 Publications/Presentations

Publications

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Presentations

1. C.M. Brown, "From metal hydrides to physisorbed H₂-systems: what we are learning with neutrons", Metal Hydrogen-Metal Systems Gordon Conference, July 2009, Lucca, Italy. *Invited*
2. J.-H. Her, Y. Liu, C.M. Brown, M. Yousufuddin, T.J. Udovic, and D.A. Neumann, "Structural Studies on Various hydrogen Storage Materials: MIL-53, K₂Zn₃[Fe(CN)₆]₂ and Li₂B₁₂H₁₂" named Outstanding Poster Presentation in Materials category at the 16th annual Postdoctoral Poster Competition sponsored by the NIST chapter of Sigma Xi, Gaithersburg, MD, Feb. 2009.

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IV.C.1p Multiply Surface-Functionalized Nanoporous Carbon for Vehicular Hydrogen Storage

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Contract Number: DE-FG36-08GO18142

Subcontractor:

Midwest Research Institute, Kansas City, MO

Project Start Date: September 1, 2008

Project End Date: January 31, 2012

Objectives

- Fabricate high-surface-area, multiply surface-functionalized carbon ("substituted materials") for reversible hydrogen storage with superior storage capacity (strong physisorption).
- Characterize materials and storage performance. Evaluate efficacy of surface functionalization, experimentally and computationally, for fabrication of materials with deep potential wells for hydrogen sorption (high binding energies).
- Optimize gravimetric and volumetric storage capacity by optimizing pore architecture and surface composition ("engineered nanospaces").

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) System Weight and Volume
- (B) System Cost

- (E) Charging/Discharging Rates
- (J) Thermal Management
- (P) Lack of Understanding of Hydrogen Physisorption and Chemisorption

Technical Targets

This project aims at the development of surface-engineered carbons, made from corncob or other low-cost raw materials, which simultaneously host high surface areas, created in a multi-step process, and a large fraction of surface sites with high binding energies for hydrogen, created by surface functionalization with boron, iron, and lithium. Targets are surface areas in excess of 4,500 m²/g, average binding energies in excess of 12 kJ/mol, and porosities below 0.8, toward the design of materials that meet the following 2015 DOE hydrogen storage targets:

- Gravimetric storage capacity: 0.055 kg H₂/kg system
- Volumetric storage capacity: 0.040 kg H₂/liter system

Accomplishments

- Manufactured a porous carbon with gravimetric excess adsorption of 0.073 ± 0.003 kg H₂/kg, gravimetric storage capacity of 0.106 ± 0.005 kg H₂/kg carbon (including gas in pore space), and volumetric storage capacity of 0.040 ± 0.002 kg H₂/liter carbon, at 80 K and 50 bar. Validated H₂ uptake measurements by measurements on a standard carbon reference sample, AX-21 MSC-30.
- Analyzed gravimetric excess adsorption isotherms at 80 K on porous carbons in terms of high/low binding energy sites in sub/supra-nm pores, respectively. Found, from Grand Canonical Monte Carlo (GCMC) simulations of adsorbed H₂ in bimodal distributions of such pores, that isotherms up to ~30 bar could successfully be modeled with binding energies of ~9 kJ/mol and ~5 kJ/mol, respectively. The simulations identified significant contributions to the isotherms from multilayers of H₂ in supra-nm pores. Above 30 bar, experimental isotherms were found to rise higher than simulated isotherms, consistent with the presence of binding energies lower than 5 kJ/mol.
- Computed adsorption potentials for boron-substituted graphene from first principles and obtained binding energies (well depths) of 12 kJ/mol for 10 wt% boron. GCMC simulations on the substituted carbon predicted gravimetric and volumetric storage capacities of 0.050 kg H₂/kg

carbon and 0.032 kg H₂/liter carbon, at 298 K and 100 bar.

- Developed analytic relation between gravimetric and volumetric storage capacity, at constant gravimetric excess adsorption. Found that volumetric capacity can be increased significantly, under an insignificant loss of gravimetric capacity, by decreasing the porosity of the adsorbent.

Introduction

High-surface-area carbons from corncob, as developed by our team, show considerable promise for reversible onboard storage of hydrogen at high gravimetric and volumetric storage capacity. A current carbon has a gravimetric storage capacity of 0.11 kg H₂/kg carbon at 80 K and 50 bar. This project is a systematic effort to achieve comparable results at 300 K, by increasing surface areas from currently ~3,000 m²/g to ~5,000 m²/g, and substituting carbon with boron and other elements that increase the binding energy for hydrogen. Current high surface areas and high binding energies are hosted by sub-nm pores (“nanopores”) created by chemical means. New surface area, created by fission tracks from boron neutron capture, $^{10}\text{B} + ^1_0\text{n} \rightarrow ^7_3\text{Li} + ^4_2\text{He}$ (U. Missouri Research Reactor), traversing stacks of graphene sheets, will add as much as another 3,000 m²/g. Thus boron serves in two functions: (i) raise the binding energy by electron donation from H₂ to electron-deficient B; (ii) provide the platform for creation of additional surface area.

Approach

The approach is an integrated fabrication, characterization, and computational effort. Structural characterization includes determination of surface areas, pore-size distributions, and pore shapes. Storage characterization includes measurements of hydrogen sorption isotherms and isosteric heats. Computational work includes adsorption potentials and simulations of adsorbed films for thermodynamic analysis of experimental isotherms. Comparison of computed and experimental isotherms validates theoretical adsorption potentials and experimental structural data.

Results

Figure 1 shows results for hydrogen excess adsorption on: (i) two porous materials, 3K and 4K, made by us, at 80 K; (ii) a standard carbon reference/calibration sample, AX-21 MSC-30 (courtesy of the National Renewable Energy Laboratory), at 77 K and 80 K; and (iii) carbon sample Anderson AX-21 at 77 K (data from [1, 2]). The results for AX-21 MSC-30 agree within error bars with published data for Maxsorb

[3] and exhibit a local maximum at $p \sim 40\text{--}50$ bar, characteristic of high-surface-area, AX-21-type carbons. (On the high-pressure side of the maximum, the density of the nonadsorbed gas grows more rapidly than the density of the adsorbed film.) By contrast, samples 3K and 4K show no such maximum in the pressure range investigated, and their excess adsorption exceeds that of AX-21 and AX-21 MSC-30. Samples 3K and 4K are members of a series of carbons, made from corncob, in which the ratio of potassium hydroxide (KOH) to carbon during chemical activation (treatment at 790°C) was varied from 2:1 (“2K”) to 6:1 (“6K”). A systematic analysis was undertaken to understand this unexpected behavior of 3K and 4K. Relevant variables for the analysis are specific surface area, porosity, pore-size distribution, gravimetric storage capacity, and volumetric storage capacity of samples (Figures 1b, c and Table 1). Storage capacity is relevant because it allows us to cross-check computed isotherms (GCMC simulations in bimodal pore-size distributions, Figure 2) for consistency with experimental results for both excess adsorption and storage capacity.

Gravimetric storage capacity, G_{st} (total mass of hydrogen stored, adsorbed film and non-adsorbed gas in pores, per mass of sample), and volumetric storage capacity, V_{st} (total mass of hydrogen stored per volume of sample), were calculated from gravimetric excess adsorption, G_{ex} (mass of excess adsorbed H₂ per mass of sample) using

$$G_{\text{st}}(p, T) = G_{\text{ex}}(p, T) + [\rho_{\text{gas}}(p, T)/\rho_{\text{skel}}]\phi/(1 - \phi), \quad (1)$$

$$V_{\text{st}}(p, T) = G_{\text{ex}}(p, T)(1 - \phi)/\rho_{\text{skel}} + \phi\rho_{\text{gas}}(p, T), \quad (2)$$

[4], where ϕ , and ρ_{skel} are porosity and skeletal density of the sample, ρ_{gas} is bulk density of H₂ gas, and p , T are pressure and temperature. If volume surrounding the sample, such as in a test bed packed with adsorbent, is included in the pore volume (any surface surrounding a solid, which may or may not include segments of the solid’s surface, defines a distinct pore volume) and porosity is evaluated accordingly, Eqs. (1, 2) automatically give the capacities of the bed. It is clear from (1, 2) that G_{st} increases and V_{st} decreases with increasing porosity. Elimination of ϕ from (1, 2) yields

$$V_{\text{st}} = \rho_{\text{gas}}/[1 - (G_{\text{ex}} - \rho_{\text{gas}}/\rho_{\text{skel}})/G_{\text{st}}], \quad (3)$$

which, for any fixed G_{ex} , describes how the volumetric capacity varies with gravimetric capacity (Figure 1c). It also describes the density ratio, $V_{\text{st}}/\rho_{\text{gas}}$, between a tank with and without adsorbent. Results (1-3) hold for any gas adsorption system and answer the question, raised by DOE, on how gravimetric and volumetric storage capacity depend on porosity.

The absence of a local maximum in samples 3K and 4K is due to variations in binding energies, and possibly vibrational frequencies of adsorbed H₂ in the

FIGURE 1. (a) Gravimetric excess adsorption isotherms of H_2 on carbon samples 3K, 4K (U. Missouri), and AX-21 MSC-30 (National Renewable Energy Laboratory), all measured on a Hiden HTP1 high-pressure volumetric analyzer (U. Missouri) at indicated temperatures. Also shown are data on carbon sample AX-21 [1, 2]. AX-21 MSC-30 was measured at 77 K for comparison with AX-21, and at 80 K for comparison with samples 3K and 4K. Experimental uncertainties are less than 5%. (b) Differential and cumulative (inset) pore-size distribution of samples AX-21 MSC-30, 3K, and 4K, determined from N_2 adsorption at 77 K and quenched solid-state density functional theory (Quantachrome Autosorb-1-C surface-area analyzer). (c) Gravimetric and volumetric hydrogen storage capacity of samples AX-21 MSC-30, 3K, and 4K, at 80 K and 50 bar (colored dots), from Table 1. The curves are plots of the volumetric vs. gravimetric storage capacity, V_{st} and G_{st} , Eq. (3), at constant gravimetric excess adsorption, G_{ex} , evaluated at 80 K, 50 bar ($\rho_{gas} = 0.016$ g/cm³), and $\rho_{skel} = 2.0$ g/cm³. Large/small values of G_{st} correspond to high/low porosity at fixed G_{ex} , Eq. (1). So V_{st} rises with decreasing G_{st} because decreasing porosity increases the volumetric storage capacity, Eq. (2). V_{st} nominally diverges when the porosity is nominally zero. The colors of the dots match the color of the nearest value of gravimetric excess adsorption. All storage capacities are material values, not system values. The 2015 DOE gravimetric and volumetric storage system targets are shown as blue area.

adsorption potential [4]. E.g., the steeper rise of excess adsorption at low pressure in sample 3K than in 4K (Figure 1a) indicates that 3K hosts a larger fraction of surface sites with high binding energies (low binding energies make the adsorbed film more compressible, which shifts the maximum of excess adsorption to higher pressures). Likewise, the slower leveling off of excess adsorption at high pressure in 4K than in 3K indicates that 4K hosts a larger fraction of sites with

low binding energies. These qualitative conclusions are supported by the data in Figures 1b and 2. Figure 1b shows that the fraction of sub-nm, high-binding-energy pores progressively decreases and the fraction of supra-nm, low-binding-energy pores increases as we go from AX-21 MSC-30 to 3K to 4K. The best fits of simulated excess adsorption isotherms, based on bimodal pore-size distributions, to the experimental data, while less than perfect, confirms this: the nominal fraction of surface

TABLE 1. Hydrogen storage on selected materials. Surface areas, from Brunauer-Emmett-Teller analysis of N_2 adsorption isotherms at 77 K and relative pressures 0.01-0.03, are rounded to the nearest hundred. Porosities were determined from N_2 adsorption at 77 K, at relative pressure 0.995. Gravimetric excess adsorption values are from Figure 1a. Gravimetric and volumetric storage capacities were calculated from Eqs. (1, 2) with $\rho_{\text{skel}} = 2.0 \text{ g/cm}^3$.

	AX-21 MSC-30	3K	4K
Ratio KOH:C for chemical activation	N/A	3:1	4:1
Specific surface area (Σ)	3,400 m^2/g	2,500 m^2/g	2,600 m^2/g
Porosity (ϕ)	0.81	0.78	0.81
Gravim. H_2 excess (G_{ex} ; 80 K, 50 bar)	0.057 kg/kg	0.069 kg/kg	0.073 kg/kg
Gravim. H_2 stored (G_{st} ; 80 K, 50 bar)	0.090 kg/kg	0.097 kg/kg	0.106 kg/kg
Volum. H_2 stored (V_{st} ; 80 K, 50 bar)	0.034 kg/liter	0.043 kg/liter	0.040 kg/liter
Density ratio, $V_{\text{st}}/\rho_{\text{gas}}$ (80 K, 50 bar)	2.2	2.7	2.6

sites with binding energy $\sim 9 \text{ kJ/mol}$ drops from 65% to 10% to 5% (Figure 2). Best fits of simulations to the low-pressure part of the isotherms only, $p \sim 0\text{--}30 \text{ bar}$, gave very good agreement with experimental data, both for excess adsorption and storage capacity, with binding energy of $\sim 9 \text{ kJ/mol}$ on 20% of surface sites, both for 3K and 4K (not shown). However, above 30 bar, the experimental isotherms were found to exceed the simulated ones. This led to the conclusion that the absence of a local maximum in samples 3K and 4K is due to a significant presence of binding energies less than 5 kJ/mol , presumably located at edge sites of fragments of graphitic sheets. The significant fraction of supra-nm pores in 3K and 4K (Figure 1b) is consistent with a significant fraction of such edge sites. The mechanism by which supra-nm pores can give rise to higher excess adsorption than sub-nm pores (Figure 1a), even though binding energies may be low, is multilayer adsorption by attractive $H_2\text{--}H_2$ interactions, effective at low temperature and in wide pores [5], but ineffective in sub-nm pores, too narrow to hold multilayers.

Figure 2 details the high gravimetric storage capacity of samples AX-21 MSC-30, 3K, and 4K at 80 K over the entire pressure range. In Figure 1c, the storage capacities are shown at 50 bar and 80 K and illustrate the nonlinear dependence of volumetric capacity on gravimetric capacity. E.g., the volumetric storage capacity – or, equivalently, the density ratio of adsorbed to compressed H_2 , $V_{\text{st}}/\rho_{\text{gas}} \sim 2.5$ (Table 1) – could be raised significantly by reducing the porosity, at an insignificant loss of gravimetric storage capacity.

Boron-substituted carbons were made from samples 3K and 4K by sublimation of decaborane ($B_{10}H_{14}$) on the

FIGURE 2. Gravimetric excess adsorption and gravimetric storage capacity of H_2 on (a) sample AX-21 MSC-30 at 77 K, (b) sample 3K at 80 K, and (c) sample 4K at 80 K (experimental, full symbols), and GCMC simulations at 77 K (open symbols) on model carbons with a bimodal distribution of slit-shaped pores and specific surface area equal to the experimental area. The slit widths, between centers of carbon atoms on opposite walls, were fixed at 0.7 nm (D7, sub-nm pores, binding energy $\sim 9 \text{ kJ/mol}$) and 2.0 nm (D20, supra-nm pores, binding energy $\sim 5 \text{ kJ/mol}$). The single fitting parameter in each simulation was the fraction of surface area in 0.7 nm pores (the remaining fraction being the surface area in 2.0 nm pores). The fractions reported gave the best fits for excess adsorption over the whole range of pressures.

surface and subsequent thermolysis of the decaborane and annealing. Analyses of surface areas and pore-size distributions before and after substitution demonstrated that boron concentrations up to 10 wt% can be brought into pores of high-surface-area carbons from outside in this way without compromising large surface areas. Investigations of H_2 adsorption on these substituted materials are underway.

To generate systematic models of H_2 storage on boron-substituted carbons as a function of boron

concentration and distribution of boron on the surface, we computed adsorption potentials for boron-substituted graphene from first principles and performed GCMC simulations of H_2 adsorption in these potentials. Results are shown in Figure 3 [6]. Boron substitution creates potential wells with binding energy (well depth) of $\sim 5, 8, 9$, and 12 kJ/mol for 0, 1, 5, and 10 wt% boron, respectively (Figure 3a, b). The simulations predict gravimetric and volumetric storage capacities of 0.050 kg H_2 /kg carbon and 0.032 kg H_2 /liter carbon for 10 wt%

FIGURE 3. Adsorption potentials for H_2 on a boron-substituted graphene sheet containing (a) 1 wt% boron (8 boron atoms), and (b) 5 wt% boron (40 boron atoms). The potentials were computed from second-order Møller-Plesset perturbation theory applied to restricted open-shell Hartree-Fock wave functions. Binding energies range from 5 kJ/mol (pink grey, "carbon") to 9 kJ/mol (dark blue, "boron"). (c) Simulated gravimetric (left axis) and volumetric (right axis) H_2 storage capacities on boron-substituted carbon, with slit-shaped pores of width 1.2 nm, as a function of boron concentration and temperature. (d) Volumetric vs. gravimetric storage capacities of boron-substituted carbons at 298 K and 100 bar, as a function of pore width (different points with same color) and boron concentration (different colors), and in relation to the 2015 DOE volumetric and gravimetric storage system targets. The curves are statistical-mechanical, isoconcentration versions (constant boron concentration) of the curves in Figure 1c. In comparison, the curves in Figure 1c, Eq. (3), are effective-medium, isosteric treatments (constant gravimetric excess adsorption) of volumetric vs. gravimetric storage capacity. The steep rise of V_{st} at low G_{st} here is the analogue of the steep rise of V_{st} in Figure 1c.

boron, 298 K, and 100 bar (Figure 3c). Gravimetric and volumetric storage capacities for variable boron concentration, 298 K, and 100 bar are presented in Figure 3d.

Conclusions and Future Directions

- Assessed that gravimetric excess adsorption isotherms at 80 K on new high-performance carbons, 3K and 4K, unlike AX-21-type carbons, do not exhibit a local maximum in the pressure range 0-100 bar, are significantly higher than excess adsorption of AX-21-type carbons, and give rise to gravimetric and volumetric storage capacities at 80 K and 50 bar which are competitive with those of MOF-177 (~0.10 kg H₂/kg adsorbent).
- Explained this performance in terms of coexistence of binding energies of ~9 kJ/mol in sub-nm pores, of ~5 kJ/mol in supra-nm pores, and of less than 5 kJ/mol on edge sites of locally graphitic sheets, and multilayer adsorption of H₂ in such pore systems.
- Assessed resulting gravimetric and volumetric storage capacities in terms of engineerable gravimetric excess adsorption and porosity (approximately independent design variables).
- Developed roadmap for achievement of comparable storage capacities at room temperature on boron-substituted carbons.
- Future work: study performance of boron-substituted materials as a function of deposition conditions of decaborane and thermal annealing; compare results with other methods of introducing boron; measure isosteric heats of adsorption and compare with results from simulations; study chemical nature of substituted boron by solid-state nuclear magnetic resonance and X-ray photoelectron spectroscopy.

FY 2009 Publications/Presentations

1. 2009 DOE Hydrogen Program Review, Washington, D.C., May 18-22, 2009. Presentation ST31.
2. L. Firlej, S. Roszak, B. Kuchta, P. Pfeifer, and C. Wexler, "Enhanced Hydrogen Adsorption in Boron Substituted Carbon Nanospaces." Submitted, July, 2009.
3. B. Kuchta, L. Firlej, P. Pfeifer, and C. Wexler, "Numerical Estimation of Hydrogen Storage Limits in Carbon Based Nanospaces." *Carbon* **47** (2009), doi: 10.1016/j.carbon.2009.09.009.

4. M. Kraus, M. Beckner, J. Burrell, J. Ilavsky, C. Wexler, and P. Pfeifer, "Hierarchical Pore Structure Analysis of Engineered Carbon Nanospaces," 5th International Workshop on Characterization of Porous Materials, Rutgers University, New Brunswick, June 24–26, 2009.

5. B. Kuchta, L. Firlej, R. Cepel, P. Pfeifer, and C. Wexler, "Structural and Energetic Factors in Designing a Perfect Nanoporous Sorbent for Hydrogen Storage." 5th International Workshop on Characterization of Porous Materials, Rutgers University, New Brunswick, June 24–26, 2009.
6. M. Beckner, J. Burrell, C. Wexler, Z. Yang, F. Hawthorne, and P. Pfeifer, "Boron-Doped Carbon Nanospaces for High-Capacity Hydrogen Storage." 2009 March Meeting of the American Physical Society, Pittsburgh, PA, March 16–20, 2009. Abstract: *Bull. Am. Phys. Soc.* **54**, W27.00010 (2009).
7. J. Burrell, M. Beckner, N. Kullman, R. Cepel, C. Wexler, and P. Pfeifer, "Analysis of Hydrogen Adsorption in Engineered Carbon Nanospaces." 2009 March Meeting of the American Physical Society, Pittsburgh, PA, March 16–20, 2009. Abstract: *Bull. Am. Phys. Soc.* **54**, W27.00012 (2009).
8. M. Kraus, M. Beckner, J. Burrell, and P. Pfeifer, "Ultra-Small-Angle X-Ray Scattering of Nanoporous Carbons." 2009 March Meeting of the American Physical Society, Pittsburgh, PA, March 16–20, 2009. Abstract: *Bull. Am. Phys. Soc.* **54**, W27.00011 (2009).
9. B. Kuchta, L. Firlej, R. Cepel, P. Pfeifer, and C. Wexler, "Structural and Energetic Factors in Designing a Perfect Nanoporous Sorbent for Hydrogen Storage." 2009 March Meeting of the American Physical Society, Pittsburgh, PA, March 16–20, 2009. Abstract: *Bull. Am. Phys. Soc.* **54**, W27.00014 (2009).
10. J. Romanos, R. Cepel, M. Beckner, M. Kraus, J. Burrell, and P. Pfeifer, "Magnetic Properties of High-Surface-Area Carbons and their Effect on Adsorbed Hydrogen." 2009 March Meeting of the American Physical Society, Pittsburgh, PA, March 16–20, 2009. Abstract: *Bull. Am. Phys. Soc.* **54**, W27.00009 (2009).

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IV.C.2 Carbide-Derived Carbons with Tunable Porosity Optimized for Hydrogen Storage

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Subcontractor:
Drexel University, Philadelphia, PA

Project Start Date: October 1, 2004
Project End Date: September 30, 2009

is working towards the former 2010 system targets including capacity targets of 6 percent hydrogen by weight and 45 grams hydrogen per liter.

Accomplishments

- Addressed the issue of volumetric capacity of CDCs processed as powders, compacting them by rolling peels or pressing pellets; the best value to date (material only) is 29 g H₂/liter.
- Also showed that chlorination of bulk ceramic monoliths preserve the excellent properties obtained from powders, along with substantial improvement in volumetric capacity.
- Found that activation of CDCs by potassium hydroxide or CO₂ increases the gravimetric capacity by as much as 30%, increasing the number of candidates for further optimization.
- Showed convincingly that pores <1 nm dominate the storage capacity over a range of pressures from 1 bar to 40 kbar; larger ones are less effective and mostly degrade the volumetric capacity.
- Determined that non-cubic Mo₂C yields CDCs with performance rivaling those obtained with the cubic precursors TiC and SiC. This observation must be accounted for in any complete model of CDC formation.
- Showed that preceramic polymers, after pyrolysis and chlorination, yield a novel form of CDC with hierarchical porosity on several length scales, providing another synthetic path to property optimization and new applications.
- Obtained first results from neutron scattering and Hybrid Reverse Monte Carlo analysis, showing that realistic atom-scale models for CDCs can be thus obtained. An optimized 2,000-atom model for TiC-CDC chlorinated at 800°C reveals complex pore shapes which bear little resemblance to the generally-assumed slit pores based on a graphite model.
- Incremental improvements in performance metrics yield optimized materials which still fall short of the 2010 capacity goals by 15% (gravimetric) and 20% (volumetric), and only at high pressure and low temperature. Further gains will only be achieved by increasing total volume of sub-nm pores and increasing enthalpies of sorption by various doping schemes e.g. Kubas interaction. Our efforts to advance along these directions have been unsuccessful.

Objectives

- Develop and demonstrate reversible hydrogen storage in carbide-derived carbons (CDCs).
- Determine the optimum pore size for hydrogen storage.
- Design a CDC that meets DOE performance targets and commercialize it.

Technical Barriers

This project addresses the following technical barriers from the Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) System Weight and Volume
- (P) Lack of Understanding of Hydrogen Physisorption and Chemisorption
- (Q) Reproducibility of Performance

Technical Targets

This project is conducting fundamental studies of CDCs for onboard hydrogen storage. This project

Introduction

Carbon supports a large number of novel structures with large surface area, e.g., activated carbon, fullerenes, carbon nanotubes, etc. An isolated flat graphene sheet has a specific surface area (SSA) of 2,600 m²/gram, but the enthalpy of *physisorption* is so low that reversible H₂ storage would require a combination of low temperature and high pressure. First-principles calculations indicate that *chemisorption* on pores with small radii of curvature is possible, but reversibility of sorption/desorption is doubtful and would require high temperature operation to liberate H₂.

Thus our agenda for achieving practical carbon-based storage materials includes the following elements: a) discover materials with tunable and large pore volume, total surface area and optimized pore size and shape to take maximum advantage of C-H₂ interactions without introducing wasted volume; b) chemical treatments of the internal pore surface to increase binding enthalpy and facilitate operation near 300 K; and/or c) introduce small concentrations of appropriate metal dopants to achieve the same purpose *via* tailored orbital hybridization.

Approach

An excellent material family for this agenda is nanoporous CDC, prepared by selective etching of crystalline carbides with chlorine gas in the range 300–1,200°C. Because the rigid metal carbide lattice is used as a template and the metal is extracted layer-by-layer, atomic-level control can be achieved in the synthesis process and the carbon structure can be templated by the carbide structure. We first confirmed experimentally that, relative to well-known activated carbons, CDCs indeed possess many advantages for hydrogen storage, such as narrow, zeolite-like pore size distributions (PSD) tunable with better than 0.05 nm sensitivity in the range ~0.5 to ~1.5 nm, SSA up to 2,000 m²/g, and ~80% open pore volume. With this point of departure we designed a series of systematic studies along several different directions, targeting increases in SSA, optimization of PSD and pore size, and if possible enhancement of the enthalpy of adsorption on pore surfaces.

Results

Importance of Pore Size in High-pressure Hydrogen Storage by Porous Carbons

Development of high-capacity hydrogen-storage systems utilizing *physisorption* at high pressure and low temperature is hindered by poor understanding

of the pore size/shape requirements for achieving the maximum hydrogen uptake. Tuning the carbon structure and pore size of CDCs with high accuracy by using different starting carbides, chlorination temperatures and activation temperatures allows rational design of carbon materials with increased hydrogen-storage capacity. Systematic experimental investigation of a large number of CDCs with controlled pore size distributions and SSA shows that pores larger than 1.5 nm contribute little to hydrogen storage. It has been experimentally demonstrated that, just as at ambient pressure, pores of 0.6–0.7 nm in diameter provide the largest H₂ uptake per unit SSA at elevated pressures and liquid nitrogen temperatures. The effect of pore size was stronger than the effect of surface chemistry on the hydrogen uptake.

Nanoporous carbons with tunable pore size and SSA up to 3,000 m²/g available for hydrogen storage have demonstrated a gravimetric hydrogen-storage density of 4.7 wt% at elevated pressure obtained either with TiC chlorinated at 600°C activated under CO₂ or low temperature synthesized CDCs (400 or 500°C) activated under KOH. While small pores (1 nm or below) are efficient for hydrogen sorption and lead to an increased heat of adsorption, mesopores do not contribute much to storage of hydrogen under these conditions. Annealing of samples has shown that the pore size effect is stronger than that of functional groups on the carbon surface. A higher SSA and larger pore volume increase the hydrogen uptake for a given pore size. Our findings provide guidance for optimal design of carbon materials for high-pressure hydrogen storage at cryogenic temperatures by realizing that a large volume of small open pores with narrow size distribution is the key to high hydrogen uptake.

CDCs with Hierarchical Porosity from a Preceramic Polymer

Synthesis of carbon by extraction of metals from carbides has been successfully used to produce a variety of microporous CDCs with narrow pore size distributions and tunable sorption properties. This approach is of limited use when larger mesopores are targeted, however, because the relevant synthesis conditions yield broad pore size distributions. Here we demonstrate the porosity control in the 3–10 nm range by employing preceramic polymer-derived silicon carbonitride (SiCN) precursors. Polymer pyrolysis in the temperature range 600 to 1,400°C prior to chlorine etching yields disordered or graphitic CDC materials with surface area in the range 800 to 2,400 m²/g. In the hierarchical pore structure formed by etching SiCN ceramics, the mesopores originate from etching silicon nitride (Si₃N₄) nano-sized crystals or amorphous Si-N domains, while the micropores come from silicon carbide (SiC) domains. The etching of polymer-derived ceramics allows synthesis of porous materials with a

very high specific surface area and a large volume of mesopores with well controlled size, which are suitable for applications as sorbents for proteins or large drug molecules, and supports for metal catalyst nanoparticles.

CDCs from SiCN ceramics (SiCN-CDCs) were produced by chlorination at 900°C or 1,200°C. Si and N are eliminated as SiCl_4 and N_2 , leaving behind a nanoporous network of > 98% pure carbon. Incomplete chlorination occurs at 600 and 800°C. Two types of etching reactions occur, depending on the microstructure of the SiCN ceramics, which in turn is controlled by pyrolysis temperature. At 600 to 1,200°C, pyrolysis of amorphous SiCN occurs via the decomposition reaction $2\text{SiC}_x\text{N}_y + 4\text{Cl}_2(\text{g}) \rightarrow 2\text{SiCl}_4(\text{g}) + y\text{N}_2(\text{g}) + 2x\text{C}(\text{s})$, while in the $\text{SiC}/\text{Si}_3\text{N}_4$ nano-composite pyrolyzed at 1,400°C, these reactions occur instead: $\text{SiC} + 2\text{Cl}_2(\text{g}) \rightarrow \text{SiCl}_4(\text{g}) + \text{C}(\text{s})$ and $\text{Si}_3\text{N}_4 + 6\text{Cl}_2(\text{g}) \rightarrow 3\text{SiCl}_4(\text{g}) + 2\text{N}_2(\text{g})$. In both cases Si and N are leached out, and C atoms self-organize into an amorphous or disordered, mainly sp²-bonded, structure. The characteristics of the mesoporosity can be controlled by varying the pyrolysis temperature, as this affects the microstructure of the ceramic material at the nano-scale. In the etching reaction of the nanocomposite pyrolysis products, SiC leaves behind carbon atoms, and Si_3N_4 completely disappears, giving rise to the formation of larger pores (mesopores) and higher pore volumes.

In conclusion, chlorine etching of amorphous or crystalline polymer-derived SiCN ceramics afford CDCs possessing both micropores and mesopores with mean pore size controllable in the range 3-10 nm with Brunauer-Emmett-Teller (BET) surface area up to 2,400 m²/g. Microstructural investigations show that SiCN remains homogeneous and amorphous up to a pyrolysis temperature of 1,200°C, above which nano-crystals of Si_3N_4 , SiC and graphite begin to form. Micropores formed by etching Si atoms from the SiC phase, while mesopores derive from the elimination of Si-N moieties. The resulting porosity (pore size, PSD, and SSA) strongly depend on pyrolysis temperature of the preceramic polymer, as well as on etching conditions. The mean pore size increases with increasing pyrolysis temperature. On the other hand, etching temperatures higher than the pyrolysis temperature do not affect the mean pore size, but leads to large BET surface area owing to the high purity. This approach can be applied to the production of porous carbon materials with very high specific surface area and large mesopore volume, potentially suitable for applications such as enterosorbents, absorption of proteins, and catalyst supports for metal particles.

Hybrid Reverse Monte Carlo Simulations of Nanoporous Carbons

In order to develop an understanding of the link between the microstructures of microporous carbons

and their physical properties, a reconstructive reverse Monte Carlo simulation technique known as Hybrid Reverse Monte Carlo (HRMC) has been developed. It generates realistic molecular models of microporous carbon structures from experimental diffraction data. Unlike its predecessors, the HRMC method uses a many-body potential in conjunction with the reverse Monte Carlo routine to simultaneously minimize the error in fit to experimental diffraction data and the total energy of the system. This assures that resulting models capture the correct chemistry, minimizing the presence of thermodynamically unstable structures such as three and four member carbon rings.

We first applied HRMC to the well-studied TiC-CDC chlorinated at 800°C, for which a wealth of comparative data is in hand. The radial distribution function reproduced the measured neutron diffraction very accurately. In particular, unphysical high energy structures such as 3 and 4 member rings were totally absent. The pore microstructures observed in 2,000-atom models were heterogeneous, with a wide range of pore sizes with complicated pore geometries. Adsorption isotherms showed typical type I behavior expected for microporous solids.

Conclusions

- Purified CDCs subjected to chemical or physical activation equal or slightly exceed, gravimetric capacity of activated carbons.
- Large pores ($d > 1.5$ nm) are less effective than small ones, both at high and low pressure.
- Bulk ceramics as well as preceramic polymers can be used as precursors for CDC synthesis, along with the more common metal carbide powders. This added flexibility provides a broader synthetic palette for optimizing CDCs with particular applications in mind.
- Spinoff startup Y-Carbon licensed to scale-up CDC manufacturing.
- Atomic-level pore structure can be found by neutron scattering and hybrid reverse Monte Carlo analysis (with Los Alamos National Laboratory and North Carolina State University).

Special Recognitions & Awards/Patents Issued

1. The editors of Technology Review magazine named Dr. Ranjan Dash one of this year's TR35, a group of the world's top young innovators. He will be profiled in Technology Review.
2. Y-Carbon (<http://www.y-carbon.us/>) has received two SBIR Phase 1 grants from NSF and ONR, and a \$50,000 grant from Ben Franklin Technology Partners.
3. Drexel University and Y-Carbon received a 2009 R&D 100 Award for Tunable Nanoporous Carbon. The

company was founded by Trustee Chair Professor Yury Gogotsi, Dr. Gleb Yushin (currently with Georgia Tech) and Dr. Ranjan Dash to develop and commercialize nanoporous carbon processing technology.

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IV.C.3 Nanostructured Activated Carbon for Hydrogen Storage

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Contract Number: DE-FG36-05GO15009

Subcontractor:

PoroGen, LLC, Boston, MA

Start Date: May 2, 2005

Projected End Date: June 30, 2010

(C) Efficiency

(E) Charging/Discharging Rate

(P) Lack of Understanding of Hydrogen Physisorption
and Chemisorption

(Q) Reproducibility of Performance

Technical Targets

The research and development of novel high surface area nanostructured carbons for hydrogen storage has been conducted in this project. This project is applied toward the synthesis of inexpensive carbon-based, high surface area sorbents that can be combined with chemical-interacting organic, and/or inorganic materials, to yield high-storage materials. These new materials and concepts have been designed to meet the DOE 2015 goals concerning the production of low-cost, high specific hydrogen binding energy hydrogen storage materials.

TABLE 1. On-Board Hydrogen Storage System Targets

Storage Parameter	Units	2015 System Target	SUNY-Syracuse**
System Gravimetric Capacity	kWh/kg (wt% H ₂)	1.8 (5.5 wt%)	2.4 (7.2 wt%)
System Volumetric Capacity	kWh/L (gH ₂ /L system)	1.3 (40)	1.2 (40)
Min/Max Delivery Temperature	K	233 – 358	77
Max delivery Pressure	bar	100	60

** Data is based on material only, not system value

Objectives

Develop and demonstrate reversible nanostructured activated carbon hydrogen storage material which has at least a 5.5 wt% materials-based gravimetric capacity and a 40 gH₂/L material-based volumetric capacity at 235–358 K, and potential to meet the DOE 2015 system-level targets.

- Prepare and characterize nanostructured polymer derivatives as carbon precursors.
- Initiate the production of nanostructured activated carbon for hydrogen storage.
- Develop methods for sorbent-based doped polymer/carbon.

Technical Barriers

This project addresses the following On-Board Hydrogen Storage Technical Barriers section (3.3.4) outlined in the Hydrogen, Fuel Cells and Infrastructure Multi-Year Research, Development and Demonstration Plan:

(A) System Weight and Volume

Accomplishments

- Established the correlation of structures (surface area and micropore volume) of the carbons with hydrogen storage capacity; an average surface coverage $\sim 16.0 \mu\text{g H}_2/\text{m}^2$ and hydrogen density in pores $\sim 0.055 \text{ g/cm}^3$ has been achieved.
- Synthetic method for incorporation of unsaturated functionalized polycyclic complexes (Melem, F-Melem, Ni-Melem) has been developed, and hydrogen binding energy has been improved to $\sim 14 \text{ kJ/mol}$.
- Achieved synthesis of modified polymer-based carbons with high surface area (up to $4,000 \text{ m}^2/\text{g}$) and low average pore width (down to $8.5 \text{ \AA}$).
- Achieved a durability of hydrogen storage on high surface area poly(ether ether ketone) (PEEK)

carbon >30 cycles with gravimetric storage capacity of ~6.7-7.4 wt%, and volumetric capacity of ~45 g/L at 77 K and 5-6 MPa.

Introduction

State University of New York-esf and PoroGen, LLC, have initiated a collaborative effort to develop superior high surface area nanostructured carbons for hydrogen storage. Synthesis of the carbon starts with the preparation of a nanoporous semicrystalline oriented polymer precursor having nanosize pores, with a uniform pore size distribution. This semicrystalline nanoporous polymer precursor is subsequently tailored to form high surface area activated carbons with slit-like micro porous structure (pore width ~7-20 Å). The high surface area of the polymeric precursor aids in preparation of this unique carbon (Bruner-Emmett-Teller [BET] specific surface area [S_{BET}] >3,000 m²/g) and enables doping initial material with chemical agents, which, upon carbonization, introduces specific interaction sites that significantly increase the hydrogen storage capacity of the nanostructured carbon material.

Approach

To achieve the project objectives, polymer-based nanostructured carbons have been synthesized by engineering the structure of the polymer precursors as to produce carbon with the designed morphology for activation to high surface area and controlled micropores. Thus, polymer precursors such as modified poly(phenylene oxide), modified PEEK, and poly(etherimide) are spun at high melt shear rates further to controlled the morphology and orientation of crystalline regions. High orientation of polymer chains and alignment of crystalline lamellar regions leads to the formation of a porous material from oriented nano-size pores that upon carbonization, with specific activation agents, produce high surface area, high microporosity activated carbon. Consequently, procedures (including parameters such as heating rate, temperature and time) were developed to properly carbonize polymer precursors. In the activation (pore creation) step, the activation kinetics, including the reactivity size of activation agents, and the homogeneity of activation system, were addressed as to control the carbons texture. The synthetic methods are expanded to incorporation reactive sites into the carbon nanostructures by doping polymerized unsaturated functionalized polycyclic complexes (Melem, F-Melem, Ni-Melem) or modification of carbon surface by solvent/polymer carbon alloy. Extensive physisorption and chemisorption (H₂ adsorption) characterizations have been performed to verify the synthetic effort.

Results

In Fiscal Year 2009, the main focus remained exploration of new materials and synthetic routes by tailoring the morphology of polymer precursor to produce high surface area, higher microporosity and small pore size nanostructured carbons. More than 100 batches of polymer-based nanostructured carbons were synthesized and screened. Figure 1 illustrates the correlation of surface area with hydrogen storage capacity at 77 K and 0.1 MPa. Two distinct regions were observed. For carbon with $S_{\text{BET}} \leq 1,300$ m²/g, hydrogen adsorption increases linearly with S_{BET} up to $W_{\text{ad.H}_2} \sim 2.7$ wt%, at an average surface coverage ~ 16.0 $\mu\text{g H}_2/\text{m}^2$. For the carbons with $S_{\text{BET}} > 1,300$ m²/g, the hydrogen uptake overall shows a modest increase with surface area. The variation of hydrogen uptake at 77 K and 0.1 MPa with total pore volume was presented in Figure 2. The hydrogen uptake is shown to increase with pore volume, but with great scatter. The calculated hydrogen density in pores varies from 0.013 g/cm³ to 0.055 g/cm³. The hydrogen storage on these carbons has been tested for more than 30 cycles, and shows no decrease of the absorption capacity.

Hydrogen uptakes of these carbon nanostructured materials were also tested at independent institutions and national laboratories. For example: a typical

FIGURE 1. The dependence of hydrogen adsorption at 77 K and 0.1 MPa on BET surface area.

FIGURE 2. The dependence of hydrogen adsorption at 77 K and 0.1 MPa on total pore volume obtained from nitrogen sorption.

hydrogen isotherms of polymer-based carbon (MPK/PI-12) shown in the Figure 3 is measured gravimetrically on an intelligent gravimetric analyzer (pressure up to 20 bar) and volumetric technique on a high temperature pressure instrument (pressure up to 60 bar) (measurements were done at Hiden Isochema Ltd.). The results of hydrogen uptake of these carbon materials are summarized in Table 2. At 77 K and pressure of 6 MPa, the hydrogen gravimetric storage capacity, $W(H_2)$ up to 7.4 wt% has been achieved by MPK/PI-6 at 77 K and 60 bar. And this material gives a volumetric storage capacity, $V(H_2) \sim 32 \text{ g H}_2/\text{L}$. The highest volumetric capacity, $V(H_2) \sim 46 \text{ g H}_2/\text{L}$, is achieved by MPK-1 (measurements by GTI, Chicago).

The hydrogen binding energy for all carbons shown here are about -5 kJ/mol. A strategy for increasing hydrogen binding energy has been executed by introducing a large number of certain ionic sites to polymer framework. In the past year, a set of trace-organometallics (Ni) and multiheterocyclic ligand compounds that were first modelled as dopant by the Parametric Model number 3 computational method. The Melem $[C_6N_7(NH_2)_3]$ which has a planar configuration that resembles a graphite structure and is rich in electronegative nitrogen element was chosen to dope within a high surface area carbon by polycondensation reaction of carbon-nitrogen-

FIGURE 3. Hydrogen isotherms of MPK/PI-12 and MPK/PI-6 polymer-based carbons measured gravimetrically (IGA instrument, pressure up to 20 bar) and volumetric technique (HTP instrument, pressure up to 60 bar). Measurements done at Hiden Isochema Ltd., U.K.

hydrocarbon monomers at elevated temperature. The melem-doped carbon exhibits a highly microporous nature. The pore size distribution histogram of this carbon (Figure 4) reveals that all the pores fall within the micropore region (pore diameter $< 20 \text{ \AA}$). Comparison of the pore size distribution prior to and after doping clearly shows that after doping, the pore size distribution shifted to the sub-nano pore region, producing a significant portion with pores below $10 \text{ \AA}$ in diameter. The melem-doped carbon shows a sharp increase in hydrogen binding energy up to 14 kJ/mol at low hydrogen loading (Figure 4).

In addition to doping organocyclic $-CNH_n$ macromolecules to high surface area carbon to increase hydrogen bind energy, solvated carbon alloyed method was also employed to substantially increase the H_2 storage temperature. Table 3 is preliminary results of the hydrogen storage capacity and storage temperature by solvent-carbon alloys, which seems to greatly enhance the storage capacity at elevated temperatures under certain conditions. A gravimetric storage capacity of up to 6.3 wt%, and a volumetric storage capacity of up to $\sim 36 \text{ g H}_2/\text{L}$ have been recorded at $> \sim 137 \text{ K}$ by highly porous carbon, e.g., PEEK/PEI-11 alloys.

TABLE 2. Hydrogen Storage Capacity of Polymer-Derived Carbon Nanostructures

Sample	S_{BET} (m^2/g)	V_{tp} (cm^3/g)	H_2 Uptake at 77K							
			0.1 MPa		1 MPa		2 MPa		6 MPa	
			g/100g	g/L	g/100g	g/L	g/100g	g/L	g/100g	g/L
MPK-1	1,800	0.84	2.0	14	3.5	26	4.5	34	5.8	43-46
MPK-2	1,760	0.74	2.1	17	3.0	24	3.3	26	4.4	35
MPK-3	2,000	0.90	2.4	17	3.5	25	3.7	26	4.5	32
MPK-4	2,300	0.97	2.6	18	3.9	26	4.3	29	5.1	35
MPK-5	2,720	1.15	2.7	16	4.4	26	4.9	29	5.8	35
MPK/PI-1	2,110	1.03	2.8	18	4.5	29	4.8	31	5.0	33
MPK/PI-2	2,430	1.03	2.8	18	4.4	29	4.8	31	4.7	31
MPK/PI-3	2,775	1.28	2.7	15	4.7	26	5.3	30	5.4	30
MPK/PI-4	2,890	1.29	2.6	14	4.7	26	5.3	30	6.4	36
MPK/PI-5	2,935	1.36	2.6	13	4.5	24	5.1	27	5.9	31
MPK/PI-6	3,035	1.81	2.5	11	5.1	22	5.9	26	7.4	32
MPK/PI-7	3,095	1.60	2.7	12	4.8	22	5.5	26	6.4	30
MPK/PI-8	3,160	1.98	2.8	11	5.0	20	5.9	24	7.0	28
MPPO-1	3,920	2.20	2.7	10	4.8	18	5.3	20	6.4	24

FIGURE 4. Hydrogen binding energy of carbon (○) and Melem-doped carbon (◆). (Insert is pore volume distribution histogram of melem doped carbon.)

Conclusion and Future Direction

- Established correlation of hydrogen storage capacity with carbon structure (surface area and micropore volume).
- Achieved a gravimetric storage capacity ~7.4 wt% and volumetric capacity ~46 g/L at 77 K on nanostructured carbons, and a ~6.3 wt% gravimetric storage capacity at 138 K by solvent/polymer-carbon alloy method.
- Achieved a durability of hydrogen storage on high surface area PEEK carbon more than 30 cycles without decrease in hydrogen adsorption.
- Enabled doping on higher surface area carbon with organometallic compounds that exhibit rigid planar configuration and are rich of electronegative nitrogen atoms, $[\text{CNH}]_n$, and increased hydrogen binding energy up to ~14 kJ/mol.
- Continue to develop, modify, characterize and scale-up production of nanoporous polymer materials and carbons.
- Improving hydrogen binding energy by surface modification and doping with heterocyclic and heteroaromatic polymers and with trace organo catalysts.

TABLE 3. Hydrogen Storage of Solvent - Nanostructured Carbon Alloy of Various Porous Textures

Carbon	Porous Texture				Hydrogen Storage		
	S_{BET} (m^2/g)	V_{mp} (mL/g)	V_{tp} (mL/g)	d_{PR} ($\text{\AA}$)	T_{de} ($^{\circ}\text{K}$)	W_{H_2} (wt %)	V_{H_2} ($\text{g H}_2/\text{L}$)
BP2000	1,560	0.70	2.07	-	-	-	-
MPK-5	2,720	1.10	1.15	17.2	137	6.3	31.4
MPK/PI-10	2,710	1.20	1.29	18.6	137	5.6	27.9
MPK/PI-11	3,300	1.46	1.85	19.0	138	7.2	35.9

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IV.C.4 Hydrogen Storage in Metal-Organic Frameworks

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Contract Number: DE-FG36-05GO15001

Project Start Date: May 1, 2005

Project End Date: April 30, 2010

Objectives

- Implementation of "soft chemisorption": design and preparation of new metal-organic framework (MOF) with metal binding sites:
 - Impregnation of metals.
 - Low-pressure measurements at various temperatures.
- Preparation of high-surface area MOFs for isorecticular covalent organic functionalization:
 - Preparation of expanded organic link.
 - High-throughput MOF synthesis.
- Coordination with theory:
 - Prediction of binding energy.

Technical Barriers

This project addresses the following technical barriers from the Storage section (3.3.4.2) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) System Weight and Volume
- (C) Efficiency
- (E) Charging/Discharging Rates

Technical Targets

This project consists of conducting fundamental studies of MOFs. Insights gained from these studies will be applied toward the design and synthesis of hydrogen storage materials that meet the following revised DOE 2015 hydrogen storage targets:

- Volumetric density: 40 g L⁻¹
- Gravimetric density: 5.5 wt%

Accomplishments

- Synthesized new Al and Zr-MOFs with bipyridine links for isorecticular metallation.
- Developed aziridation reactions to introduce ethanediamine group (-NHCH₂CH₂NH₂) on newly prepared MOFs with amino groups.
- Began metal-doping experiments for immobilization of metal complexes.
- Environment of the metal coordination sites was studied by the extended X-ray absorption fine structure spectroscopy (EXAFS).
- Applied supercritical CO₂ drying technique for sample activation.
- Crystalline material with the lowest density as observed was prepared.

Introduction

Conventional storage of large amounts of hydrogen in its molecular form is difficult and expensive because it requires employing either extremely high pressure as a gas or very low temperature as a liquid. Because of the importance of hydrogen as a fuel, the DOE has set system targets for H₂ storage; the gravimetric (5.5 wt%) and volumetric (40 g L⁻¹) densities to be achieved by 2015. MOFs exhibit the highest hydrogen uptake of any porous materials and clearly show that the DOE targets can be achieved at 77 K. The implementation of room temperature hydrogen storage in MOF materials will require the design of new porous solids. We are therefore undertaking efforts to discover highly porous materials with strong affinity for hydrogen.

Approach

To meet the DOE 2015 system targets by physisorption, adsorbents must have high surface area (>3,000 m² g⁻¹) and relatively high density (>0.70 g cm⁻³). We have already demonstrated how to design high

surface area materials; however, in many cases these materials do not show steep H_2 uptake in the low pressure region, which is indicative of the weak interaction with H_2 . Last year, based on the relationship between adsorption enthalpy and Henry's constant, we suggest that greater adsorption enthalpy is the key issue for the improvement of H_2 uptake at room temperature. To that end, we must design MOFs that contain both strong binding sites and high surface areas. In this fiscal year, we implemented the strategy to improve the adsorption enthalpy in MOF systems.

Results

To improve the adsorption enthalpy of MOFs we believe that metal impregnation is one of the most promising strategies. At present there are at least two challenges that must be addressed for a porous MOF with strong H_2 binding sites to be realized. The first is to create metal binding sites in the MOF structures; second is characterization of coordination behavior of metals in the frameworks. In this year we prepared MOFs possessing metal binding sites by different methods. In one case we employed functionalized organic links to immobilize metal ions; in another isorecticular functionalization was used to create potential metal binding sites. These MOFs were used for successive metal impregnation experiments.

Synthesis of MOFs with Bipyridine Links – We prepared new Al- and Zr-MOF with 2,2'-bipyridine-5,5'-dicarboxylate (BPyDC) link by solvothermal synthesis. The reasons why we chose these systems are as follows: (i) two nitrogen atoms in the organic link can hold metals, while these metals do not form small molecules (e.g. $M(BPy)_3$), (ii) higher stability compared to Zn-MOFs, (iii) simple and scalable synthetic procedure, (iv) prevention of metal exchange during the metal impregnation process, and (v) relatively long ditopic link is advantageous for providing reasonable surface area and pore volume even after the metal impregnation.

The structure of Al-MOF ($[Al(OH)(BPyDC)]$, termed MOF-253) was confirmed by powder X-ray diffraction measurements and elemental analysis. The Brunauer-Emmett-Teller (BET) surface area is calculated to be $1,380 \text{ m}^2 \text{ g}^{-1}$, and its H_2 uptake at 77 K and 1 bar is 14 mg g^{-1} . To implement metal impregnation, pristine MOF-253 was immersed in the solution containing Sc(III) ion. After washing unreacted metal ions and successive drying, N_2 and H_2 isotherms were recorded for the resulting compound, termed MOF-253-Sc. As shown in Figure 1, the profile of the H_2 isotherm for MOF-253-Sc is almost the same as the pristine material, indicating that metal ions are not immobilized. Indeed, the inductively coupled plasma analysis supports this result. Next, we tried a similar impregnation reaction with excess Cr(III) and Fe(III) ions. In order to avoid leaching of metals, we only used a small amount of

FIGURE 1. Low pressure H_2 isotherms for MOF-253 and its derivatives at 77 K. (Inset) proposed metallation reaction in MOFs.

solvent to wash the sample (MOF-253-Cr and MOF-253-Fe, respectively). The H_2 isotherms for MOF-253 derivatives are illustrated in Figure 1. Although slight color change for the MOF was observed, metal salts contaminated the sample (by visual observation). Therefore, it is difficult to compare the H_2 uptake capacity of this sample to pristine MOF-253. However, given the profile of the isotherm, it doesn't seem that the Henry's constant of the isotherm is improved drastically. We will impregnate other metals such as Pt and Pd to study H_2 uptake behavior.

When $ZrCl_3$ was used as a metal source, Zr-MOF ($Zr_6O_4(OH)_4(BPyDC)_6$, termed MOF-267) was obtained. From the similarity of the powder X-ray diffraction patterns, it is presumed that the connectivity of MOF-267 is the same as UiO-67 [1]. The calculated BET surface area is $1,550 \text{ m}^2 \text{ g}^{-1}$ and H_2 uptake at 77 K and 1 bar was 11 mg g^{-1} . We plan to perform the metal impregnation experiments in the next fiscal year.

Impregnation of Ethanediamine-MOF with Metal Ions – Originally we prepared IRMOF-3 derivatives having ethanediamine group ($-NHCH_2CH_2NH_2$, terms IRMOF-3n) by isorecticular functionalization. After the modification, IRMOF-3n was immersed in the solution containing Fe(II) ions. However, the metal composition of the IRMOF-3 derivative implies that zinc ions leached out from the IRMOF and were coordinated to ethanediamine groups. Therefore, we prepared the analogous Al-based MOF ($[Al(OH)(NH_2-BDC)]$, MOF-153) to prevent unexpected side reactions. Indeed, in our preliminary analyses, MOF-153 shows higher thermal and chemical stability compared to IRMOFs, even though the surface area is not quite as high.

Addition of the ethyleneamine group was performed in toluene with excess amount aziridine. After the reaction the powder X-ray diffraction pattern was similar to the original material. We further characterized the post-modified materials by nuclear magnetic resonance

and elemental analysis. Unlike IRMOF-3, it seems that the aziridine reaction didn't occur in the cage of MOF-153. This result may be due to the smaller pore diameter of MOF-153 compared to IRMOF-3. Therefore, we prepared a new amino-functionalized MOF with larger cavity (termed MOF-202).

The topology (connectivity) of MOF-202 is the same as MIL-101 [2]. Since MOF-202 has large pore openings (>10 Å) and two types of large cages (25–30 Å), we expected that the pore aperture/diameter of MOF-202 after the reaction with aziridine would remain large enough for gas diffusion. However, the BET surface area of MOF-202n (modified material) was much smaller than that of the pristine material (2,000 and 525 $\text{m}^2 \text{g}^{-1}$ for MOF-202 and MOF-202n, respectively). The reason for the surface area decrease is not clear. Considering that powder X-ray diffraction pattern of MOF-202n is identical to MOF-202, pore openings of MOF-202n could be partly blocked by the post-modification process. We also saw by mass spectra that we had multiple additions of ethyleneamine to a single terminal amine group, resulting in an oligomer.

After modification, MOF-202n was immersed in a solution containing Cr(III) ions. Hereafter, the Cr-treated sample is termed MOF-202n-Cr. The BET surface area of MOF-202n-Cr was estimated to be 200 $\text{m}^2 \text{g}^{-1}$, which is smaller than MOF-202n probably due to the mass added as a result of metal impregnation. Figure 2 illustrates the H_2 isotherms for MOF-202n and MOF-202n-Cr measured at 77 K. The metal impregnated material shows slightly better H_2 uptake behavior in the very low pressure range; however, adsorbed H_2 amount in these MOFs are much smaller than in the pristine sample (MOF-202). This deficit indicates that higher surface area is a prerequisite for the reasonable H_2 uptake.

Based on the 77 and 87 K isotherms, the heat of adsorption (Q_{st}) of H_2 was estimated. Unexpectedly, the

FIGURE 2. Low pressure H_2 isotherms for MOF-202 and its derivatives at 77 K. (Inset) proposed metallation reaction in the ethylenediamine-MOF.

impregnated compound shows smaller Q_{st} value (7.1 kJ mol^{-1}) compared to MOF-202n (9.9 kJ mol^{-1}), indicating that there is no strong Cr- H_2 interaction in this system. We heated the sample at 200°C for 2 days to remove any solvent occluded in the pores. However, the profile of the H_2 isotherm for MOF-202n-Cr didn't change even after heating. Although it is not clear whether there are solvent molecules on Cr ions, it seems that heating is not an effective method for activation. It may be necessary to extract coordinated solvents under supercritical conditions (e.g. CO_2).

Isorecticular Metallation of MOFs – Although metal impregnation experiments were performed using two new MOFs, it is still not clear how the metals were bound to organic functionalities. The lack of the information on the metal coordination sites may hamper understanding of any metal- H_2 interaction. We chose another MOF system $((\text{Zn}_4\text{O})_3(\text{NH}_2\text{-BDC})_3(\text{BTB})_4)$ to implement the isorecticular covalent modification and successive metallation (Pd coordination). Indeed, after reaction with a palladium salt, almost 100% of metal coordination sites were occupied by palladium ions. In general it is not easy to determine the metal coordination environment within the framework based on elemental analysis and conventional X-ray diffraction techniques. Therefore, the metal coordination environment was investigated by Pd K-edge EXAFS.

Crystals of $(\text{Zn}_4\text{O})_3(\text{NH}_2\text{-BDC})_3(\text{BTB})_4$ (Figure 3, A), were reacted with 2-pyridinecarboxaldehyde to form the covalently bound iminopyridine chelate derivative, $(\text{Zn}_4\text{O})_3(\text{C}_6\text{H}_5\text{N}_2\text{-BDC})_3(\text{BTB})_4$ (B), which was reacted with $\text{PdCl}_2(\text{CH}_3\text{CN})_2$ to give the metal complexed MOF, $(\text{Zn}_4\text{O})_3(\text{C}_6\text{H}_5\text{N}_2\text{PdCl}_2\text{-BDC})_3(\text{BTB})_4$ (C). Remarkably, these reactions and their respective products are achieved without loss of structural order or framework connectivity.

FIGURE 3. Low-pressure H_2 isotherms for compound A (blue) and C (red) measured at 77 K. Molecular structures of A and C (before and after functionalization, respectively) are shown as cage structures.

The porosity of **B** and **C** was confirmed by Ar adsorption measurements at 87 K (the BET surface areas for **B** and **C** are 3,200 and 1,700 m² g⁻¹, respectively). It is worth noting that both materials maintain porosity after two subsequent chemical transformations. Additionally, Type IV isotherms are observed in all samples (**A-C**). We also note that compounds **B** and **C** were activated on the supercritical CO₂ dryer, and no sample degradation under the supercritical conditions was observed. Based on repeated use for several compounds, we conclude that supercritical CO₂ drying is the best way to activate metal impregnated samples.

Figure 3 demonstrates low-pressure H₂ isotherms for compounds **A** and **C**. H₂ uptake in **C** is 0.9 wt% at 77 K and 1 bar, which is smaller than that in **A** due to the smaller BET surface area. However, the heat of adsorption profile for **C** is improved by metallation (the Q_{st} values at zero-coverage for **A** and **C** are 5.7 and 6.6 kJ mol⁻¹, respectively). The successful isorecticular covalent transformation followed by metallation opens a route for incorporating metal ions into a wide range of frameworks. This is an important first step toward exploiting such metallated frameworks in gas-storage applications.

Isorecticular Expansion of MOFs – Isorecticular covalent functionalization and metallation is a very important strategy to enhance hydrogen density at room temperature. However, we notice that preparation of larger pore MOFs is a prerequisite for implementation of isorecticular modification without reduction of surface area. Therefore, we designed and prepared expanded structures of MOF-177 and MOF-199 with much larger unit cell parameters than original structures without changing the underlying topology by employing a longer tritopic organic link (1,3,5-tris(4'-carboxy[1,1'-biphenyl]-4-yl)-benzene, H₃BBC).

MOF-200 (Zn₄O(BBC)₂) was prepared as truncated octahedral crystals by solvothermal reaction of H₃BBC and Zn(NO₃)₂. Because of the long organic link, the cavity in MOF-200 encloses a sphere of 2.2 nm. MOF-399 has even larger pore (4.5 nm in diameter), although the organic link is the same as MOF-200. MOF-399 was prepared solvothermally by employing H₃BBC and Cu(NO₃)₂, which resulted in blue-green truncated crystals. The calculated density for MOF-399 based on the single crystal data is 0.13 g cm⁻³. This value is markedly lower than those of highly porous MOFs known previously, such as MOF-177 and 200 (0.43 and 0.23 g cm⁻³, respectively). It should be noted that the density of MOF-399 is even lower than that of COF-108 (0.17 g cm⁻³) [3], which is known as the organic crystal with the lowest density. Next year we will activate these expanded MOFs using the supercritical CO₂ dryer and examine their high pressure H₂ uptake behavior.

Conclusions and Future Directions

For room temperature H₂ storage, strong binding energy is a prerequisite. In the case of (Zn₄O)₅(C₆H₅N₂PdCl₂-BDC)₃(BTB)₄, the binding energy between metal and H₂ was improved by 15%; however, the reduction of surface area also reduces H₂ uptake capacity by 30%. This again raises the importance of high surface area materials. In the future we will perform isorecticular functionalization and metallation on high surface area MOFs to improve storage temperature of H₂.

- Employ light weight metals to create strong binding sites (e.g. potential halogen-lithium exchange).
- Use inorganic secondary building units with transition metals to create open metal sites.
- Material design based on theoretical prediction (design proximal Lewis acid-base sites).
- Supercritical CO₂ drying for ultrahigh surface area MOFs.

Special Recognitions & Awards/Patents Issued

1. The International Izatt-Christensen Award in Macrocyclic Chemistry to be presented at ISMC 2009.
2. Top 10 researchers in chemistry based on total citations.
3. ACS Award in the Chemistry of Materials.

FY 2009 Publications/Presentations

1. *Control of Vertex Geometry, Structure Dimensionality, Functionality and Pore-Metrics in the Reticular Synthesis of Crystalline Metal-Organic Frameworks and Polyhedra*, H. Furukawa, J. Kim, N.W. Ockwig, M. O'Keeffe, and O.M. Yaghi, *J. Am. Chem. Soc.* **2008**, *130*, 11650-11661.
2. *Secondary building units, nets and bonding in the chemistry of metal-organic frameworks*, D.J. Tranchemontagne, J. L. Mendoza-Cortes, M. O'Keeffe, and O. M. Yaghi, *Chem. Soc. Rev.* **2009**, *38*, 1257-1283.
3. *Isorecticular Metalation of Metal-Organic Frameworks*, C.J. Doonan, W. Morris, H. Furukawa, O.M. Yaghi, *J. Am. Chem. Soc.*, **2009**, *131*, 9492-9493.
4. *Tuning Pore Sizes in Metal-Organic Frameworks: Interpenetration and in situ Linker Formation*, D.J. Tranchemontagne, K.S. Park, H. Furukawa, J. Eckert, C. Knobler, and O.M. Yaghi, *Inorg. Chem.* to be submitted.

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IV.C.5 A Joint Theory and Experimental Project in the High-Throughput Synthesis and Testing of Porous COF and ZIF Materials for On-Board Vehicular Hydrogen Storage

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Contract Number: DE-FG36-08GO18141

Project Start Date: September 1, 2008 (funded from April, 2009)

Project End Date: January 31, 2013

(P) Lack of Understanding of Hydrogen Physisorption and Chemisorption

Technical Targets

This project consists of conducting fundamental studies of covalent organic frameworks (COFs) and zeolitic imidazolate frameworks (ZIFs). Insights gained from these studies will be applied toward the design and synthesis of hydrogen storage materials that meet the following DOE 2015 hydrogen storage system targets:

- Volumetric density: 40 g L⁻¹
- Gravimetric density: 5.5 wt%

Approach

Storage of hydrogen in porous materials is a promising approach to achieve the DOE system requirements for use of hydrogen as a transportation fuel. Since the first report of successful hydrogen storage in metal-organic frameworks (MOFs), we and others have succeeded in incrementally increasing the gravimetric and volumetric capacities to reach the highest hydrogen uptake capacity, albeit at 77 K. However, for on-board vehicular hydrogen storage it is necessary to improve the adsorption enthalpy of porous materials to achieve significant capacities at room temperature.

In this project period, we will implement metal impregnation in new classes of porous materials, COFs and ZIFs, to achieve room temperature hydrogen storage. COFs and ZIFs have the designable qualities of MOFs, but with features previously unattained in MOFs: (i) COFs are the least dense (0.17 g cm⁻³) crystalline materials known, and they are replete with six-membered carbon rings ideally suited for impregnation with electropositive dopants such as Li, Na and K, and (ii) ZIFs are replete with metal ions linked with aromatic imidazoles whose electronic character can be tuned to enhance binding of hydrogen.

We plan to implement high-throughput synthesis protocols to discover metal impregnated COFs and ZIFs, and the resulting materials will be evaluated by high-throughput characterization techniques. More importantly, we combine theory/simulation with material synthesis and characterization, which will allow our team to rapidly scan promising classes of materials.

Objectives

- High-throughput computational screening to identify new materials for favorable H₂ uptake.
- High-throughput preparation/characterization of doped materials predicted for high uptake.
- High-throughput screening to testing a diverse set of compositions and structures.
- Develop chemistry and perform computational testing of Li/Na/K doping effects on H₂ uptake.
- Predict and determine heat evolved upon reversible uptake and release.

Technical Barriers

This project addresses the following technical barriers from the Storage section (3.3.4.2) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) System Weight and Volume
- (C) Efficiency
- (E) Charging/Discharging Rates

Accomplishments

- For high-throughput COF discovery, a stainless-steel reaction plate with 24 wells was designed and prepared. Conventional COFs were successfully reproduced using this new system.
- Synthesis of new ZIFs for metal impregnation. High-pressure H_2 isotherms of ZIF-68 ($Zn(C_7H_5N_2)(NO_2-C_3H_2N_2)$), 2.7 wt% at 77 K and 35 bar) and ZIF-76 ($Zn(C_3H_3N_2)(Cl-C_7H_4N_2)$), 2.2 wt% at 77 K and 46 bar) were also recorded.
- Total H_2 uptake in Li-impregnated COF-102 ($C_{25}H_{24}B_4O_8/8Li$) at 298 K has been calculated (8.2 wt% (42 g L^{-1}) at 100 bar), which shows optimal Q_{st} values (31 - 22 kJ mol^{-1}). The amount of H_2 delivered for Li/COF-102 is 4.0 wt% (20 g L^{-1}) when the pressure ranges from 5 to 100 bar.
- Began modeling study of five new 3-dimensional COFs and predicted their H_2 uptake capacity at 77 K.

Future Directions

- Develop new force fields for modeling adsorption properties of ZIFs and COFs. Test models using reported adsorption data for a range of known ZIFs and COFs.
- Experimentally explore metal impregnation conditions in existing ZIFs and COFs, and characterize metal density in the frameworks. Compare with predictions from theory.
- Investigate pressure and temperature dependence of H_2 uptake in impregnated existing ZIFs and COFs over the parameter range specified in revised DOE 2015 guidelines (5.5 wt% and 40 g L^{-1} up to 100 bar, -30/50°C). Compare with predictions from theory.
- Discover new ZIF and COF materials utilizing high-throughput methods and explore hydrogen uptake properties of ZIFs and COFs in the same parameter range.

IV.C.6 New Carbon-Based Porous Materials with Increased Heats of Adsorption for Hydrogen Storage

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Contract Number: DE-FG36-08GO18137/A001

Project Start Date: September 1, 2008
Project End Date: August 31, 2012

Objectives

- Develop new materials to meet DOE gravimetric and volumetric targets for hydrogen storage:
 - Develop and optimize strategies for introducing cations into metal-organic frameworks (MOFs).
 - Synthesize new polymeric-organic frameworks (POFs) that contain cations.
 - Use computational modeling to understand existing materials and design new materials for hydrogen storage.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) System Weight and Volume
- (E) Charging/Discharging Rates
- (P) Lack of Understanding of Hydrogen Physisorption and Chemisorption

Technical Targets

This project is developing and testing new materials for hydrogen storage. These new materials can be applied in the future in the design of hydrogen storage systems that meet the following DOE 2010 hydrogen storage targets:

- System Gravimetric Capacity: 1.5 kWh/kg = 0.045 kg H₂/kg system
- System Volumetric Capacity: 0.9 kWh/L = 0.028 kg H₂/L system

Approach

Our approach has three strongly inter-related thrusts:

- Development and optimization of cation-doping strategies for MOFs.
- Synthesis of new, POFs that also contain cation sites.
- Computational elucidation and design as guidance and verification for experimental work.

MOFs provide an incredibly flexible platform for nanoporous materials design. They have completely uniform channels and pores of tunable diameters, and they are enormously tunable in chemical composition. In addition, MOFs have the lowest densities of any known crystalline materials. For hydrogen storage, the biggest problem is the low binding energy of hydrogen. Our main approach for overcoming this is to introduce lithium and other cations into MOFs. We are developing several methods for doing this based on 1) framework reduction, 2) synthesis of MOFs with pendant hydroxyl groups and ion-exchange of the hydroxyl H⁺ with Li⁺ or other cations, and 3) synthesis of MOFs having anionic frameworks balanced by cations.

As a complement to the MOFs, we are investigating new families of all-organic materials designed with rigid, bulky groups to prevent efficient packing of polymer chains and thus to produce microporosity and high internal surface areas. This new family of POFs can, in principle, have higher hydrogen loading capacities because their density on average is expected to be lower than MOFs. The proposed systems will have built-in functional groups which are intended to tune the enthalpy of interaction with adsorbed hydrogen. Functional groups such as -NH₂, -NH-, -OH can be

easily designed into the POFs allowing for Li^+ , Ca^{2+} , or Mg^{2+} addition and enhanced H_2 sorption.

Molecular modeling is already playing an important role in the development of MOFs. We are using a combination of quantum chemical calculations and classical grand canonical Monte Carlo simulations. Quantum chemical calculations at the MP2 level are used to elucidate how hydrogen interacts with the lithiated functional groups in MOFs and POFs, providing estimates of heats of adsorption. We will also explore other cations such as Mg^{2+} as a guide for experiments. The Monte Carlo simulations then allow prediction of adsorption isotherms, using the quantum chemical energies as inputs. Modeling can be used to screen hypothetical MOFs before they are synthesized and to provide insights that are difficult to obtain by direct experiment.

Accomplishments

The project was initiated in February 2009.

- The MOF UMCM-1- NH_2 having pendant amine groups was synthesized according to literature procedures and characterized. Subsequently, an amine hydrogen was ion-exchanged with lithium. Hydrogen adsorption measurements were carried out at 77 K and 87 K on the materials before and after lithium exchange. Hydrogen uptake at 1 atm increases from 1.07 wt% in UMCM-1- NH_2 to 1.42 wt% in UMCM-1-NH Li as shown in Figure 1.
- The isosteric heats of adsorption (q_{st}) for hydrogen were determined from the 87 K and 77 K isotherms in UMCM-1- NH_2 and UMCM-1-NH Li . The maximum q_{st} for UMCM-1- NH_2 was determined to

FIGURE 1. Hydrogen isotherms at 77 K of (a) UMCM-1- NH_2 as synthesized and (b) UMCM-1-NH Li (1.4:1 Li:amine loading). Closed symbols are adsorption, open symbols desorption.

be 5.6 kJ/mol. After lithiation the material shows a q_{st} of 6.2 kJ/mol, a significant increase. See Figure 2.

- During the last three months, microporous POFs with specific surface areas up to $900 \text{ m}^2\text{g}^{-1}$ have been developed by our group. Their synthesis is based on Schiff's base chemistry by forming imine linkages ($\text{C}=\text{N}$) from amines and aldehydes.
- Both linear and cross-linked POFs have been developed, many using inexpensive and commercially available starting materials. Synthesis conditions were optimized to obtain higher surface area and micropore volume.
- Synthesized POFs have been characterized by N_2 porosimetry to determine specific surface area, micropore volume, and total pore volume. All materials are microporous, and surface areas vary from 200 to $900 \text{ m}^2/\text{g}$ as shown in Table 1.
- The linear chain POFs with the highest surface areas and micropore volumes (POF-1, POF-2 and POF-5) were examined for hydrogen storage by volumetric adsorption of H_2 at 77 K and ambient pressure. The H_2 adsorption isotherms are presented in Figure 3. The uptake of H_2 for the samples POF-1 and -2 achieves approximately 1 wt%, and POF-5, which has the highest micropore and total pore volume, exhibits uptake around 1.5 wt%.
- We predicted adsorption isotherms for hydrogen in a diverse set of 43 MOFs using grand canonical Monte Carlo simulations. Isotherms were predicted up to 120 bar at 77 K and 298 K.
- Using the simulated isotherms, we tested simple correlations (based on surface area and pore

FIGURE 2. Hydrogen Isosteric Heats of Adsorption (q_{st}) for (a) UMCM-1- NH_2 as Synthesized and (b) UMCM-1-NH Li

TABLE 1. Porous Features of POFs

Sample Name	Specific Surface Area (m ² g ⁻¹)	Micropore Volume (cm ³ g ⁻¹)	Total Pore Volume (cm ³ g ⁻¹)
POF-1	820	0.33	0.40
POF-2	760	0.30	0.41
POF-3	625	0.23	0.43
POF-4	545	0.19	0.35
POF-5	878	0.35	0.54
POF-6	207	0.01	0.3
POF-7	919	0.31	1.13
POF-8	866	0.29	1.01
POF-9	585	0.19	0.42
POF-10	465	0.15	0.43

FIGURE 3. H₂ Adsorption Isotherms for POF-1, POF-2 and POF-5 at 77 K

volume) that could be used to very rapidly estimate hydrogen uptake in MOFs. The results indicate that hydrogen uptake at 77 K can be reliably estimated simply from the free volume for MOFs that do not contain cations.

- All of the simple correlations tested for rapidly estimating hydrogen uptake in MOFs failed at 298 K because the density of adsorbed hydrogen is low. This result underscores the main thrust of this project: significant increases in the binding energy of hydrogen will be required to increase room temperature hydrogen storage in MOFs and POFs.

Future Directions

- Additional cation-containing MOFs will be synthesized. By varying the attachment chemistry, the nature of the cation, and the solvent removal procedure, we anticipate achieving adsorption enthalpies of 10 kJ/mol.
- Hydrogen uptake in our MOFs will be measured at 298 K and up to 100 bar.
- The cross-linked POFs in hand will be analyzed for hydrogen uptake in the very near future.
- POFs will be functionalized with -OH (hydroxyl) groups, and the materials will be lithiated to increase the hydrogen uptake. We anticipate very robust materials for hydrogen storage.
- Additional POFs will be synthesized using a variety of chemistries.
- Hydrogen uptake in our POFs will be measured at 298 K and up to 100 bar.
- Quantum chemical modeling will be performed for the MOFs and POFs synthesized within this project.
- A procedure will be developed for seamlessly incorporating energies calculated quantum mechanically into classical Monte Carlo simulations. This will allow prediction of adsorption isotherms in existing and hypothetical materials. By screening a large number of materials computationally, we anticipate developing insights into how combinations of cation sites, pore sizes, and other properties should be optimized for maximum hydrogen storage near room temperature.

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IV.C.7 Hydrogen Trapping through Designer Hydrogen Spillover Molecules with Reversible Temperature and Pressure-Induced Switching

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Contract Number: DE-FG36-08GO18139

Subcontractor:
Rutgers University (RU), Piscataway, NJ

Project Start Date: January 1, 2009
Project End Date: November 30, 2011

Objectives

Synthesize designer microporous metal-organic frameworks (MMOFs) mixed with catalysts to enable H-spillover for H₂ storage at 300 K - 400 K and moderate pressures.

For year 1 (Jan-Dec. 2009) of the project:

- Explore the effect of surface chemistry, porosity, and structure on hydrogen spillover (RU, synthesis) –50% complete; (PSU, hydrogen measurements) –10% complete
- Method development for catalyst studies and MMOF compatibility with catalysts (PSU) –10% complete
- Explore the incorporation of active hydrogen dissociation centers directly into the MMOF framework – (RU synthesis) –50% complete; (PSU method development, measurements) –5% complete

Technical Barriers

This project addresses the following technical barriers from the Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) System Weight and Volume
- (D) Durability/Operability
- (E) Charging/Discharging Rates

Technical Targets

TABLE 1A. PSU/RU Progress toward Meeting DOE Targets for Hydrogen Storage (Room temperature H₂ adsorption data collected)

Characteristics	Units	2010/2015 Targets	PSU/RU Status
Gravimetric Capacity (Material)	kg H ₂ /kg System	0.045/0.055	Cu(hfipbb)H ₂ (hfipbb) _{0.5} (Figure 1) 0.0011 (20 bar; with 5%Pt/C in 9:1; Figure 1) Zn(bdc)(ted) _{0.5} (See Figure 1) 0.0027 (20 bar; with 5%Pt/C in 9:1; Figure 1) Cu ₃ (btc) ₂ (H ₂ O) ₃ (Figure 3) 0.0027 (20 bar; Figure 3; PSU) 0.004 (20 bar, RU; Figure 3v) 0.012 (60 bar; RU) ~0.02 (100 bar extrapolation, Figure 3, RU)
Operating Temperature	°C	-30 to 50/-40 to 60	25
Pressure	atm	100/100	20[PSU]/60[RU]/100[extrapolated]

Additional samples synthesized and characterized for porosity/surface chemistry studies but not yet tested for hydrogen adsorption:

- Cu(ipa)(bpy)₃H₂O
- MMOF-2-Cu and MMOF-2-Ni ([M₂(bpdc)₂(ted)]·nDMF, where M = Cu or Ni)
- MMOF-3-Zn ([Zn₂(oba)₂(bpy)]·DMF)

Additional technical issues being addressed: pressure savings over empty tank; temperature and pressure switching.

This project is conducting fundamental studies regarding hydrogen spillover, MMOF structural changes, and incorporating temperature and pressure switches into material design. Insights gained from these studies will be applied toward the design and synthesis of hydrogen storage materials that meet the DOE 2010 hydrogen storage targets outlined previously.

TABLE 1B. PSU/RU Progress toward Meeting DOE Targets for Hydrogen Storage (Low temperature H₂ physisorption data collected)

Characteristics	Units	2010/2015 Targets	PSU/RU Status
Gravimetric Capacity (Material)	kg H ₂ /kg System	0.045/0.055	Cu(hfipbb)H ₂ (hfipbb) _{0.5} 0.0028 (20 bar; Figure 1) 0.0027 (0 bar; desorption hysteresis; Figure 1) Zn ₂ (bpdcc) ₂ (bpee): 0.014 (20 bar; Figure 2) 0.0182 (70 bar, RU, not shown) Cu ₃ (btc) ₂ (H ₂ O) ₃ (Figure 3) 0.021 (1 atm; RU) Zn(bdc)(ted) _{0.5} 0.021 (1 atm; RU)
Operating Temperature	°C	-30 to 50/-40 to 60	-196 (-186)
Operating pressure	Atm	100/100	20/60/100

Results

To date, MOF materials showing H₂ trapping include:

- Cu(hfipbb)H₂(hfipbb)_{0.5} at 77 K exhibits 90% trapping as pressure (P) is reduced from 20 bar to 0 bar (Figure 1).

FIGURE 1. Low temperature H₂ adsorption data for Cu(hfipbb)(H₂hfipbb)_{0.5} (top, squares) shows significant hysteresis at 77 K, relevant to the trapping aspect of the project (gravimetric; PSU); Mixing MOFs with 5% Pt/C induces hydrogen spillover at 300 K. Increased spillover uptake for Zn(bdc)(ted)_{0.5} relative to Cu(hfipbb)(H₂hfipbb)_{0.5} is attributed to increased porosity of the former. Structures shown at right: Cu(blue), Zn (teal in top), O (red), C(grey), and F (teal in bottom).

- Zn₂(bpdcc)₂(bpee) at 87 K exhibits 35% trapping as P is reduced from 20 bar to 0 bar (Figure 2). This is dependent on equilibration time (data not shown).
- Zn₂(bpdcc)₂(bpee) at 77 K exhibits 45% trapping as P is reduced from 20 bar to 0 bar (Figure 2). This is dependent on equilibration time (see Figure 2).
- Note: Zn₂(bpdcc)₂(bpee) also shows very large hysteresis at 77 K and P < P_{sat} for Ar and N₂, which is typical of 'gate-opening' as observed by Li & Kaneko, [1].

Additional MMOFs synthesized for fundamental hysteresis studies (for both H₂ and other gases) include:

- Cu(dhbc)₂(bpy) –from Kitagawa, [2].
- Cu(bpy)(BF₄)₂(H₂O)₂·bpy–from Li & Kaneko, [1].

Approach

The term *hydrogen spillover* has been used to describe a synergistic effect between high-surface area adsorbents and associated metals. The associated metal may act to dissociate molecular H₂ into atomic H species. The atomic H is then free to migrate to surface sites on the high-surface area support; the net surface H concentration is a function of the relative rates of surface migration versus desorption from the surface. This process increases the active adsorption temperature of the high-surface area adsorbent and generally leads

FIGURE 2. H₂ isotherms for MOF sample Zn₂(bpdcc)₂(bpee), with temperature and equilibration time as labeled. All displayed data collected at PSU with a gravimetric apparatus; data were in excellent agreement with RU data collected on a volumetric system. Solid signs represent adsorption, hollow signs represent desorption. Lines are used to lead the eyes. Data suggests 40 minute equilibrium time is insufficient at 77 K for this sample. Isotherm measured for 100 min (not shown in the figure) matches 180 minute equilibration time. Hysteresis adsorption is suggestive of diffusion limitations of H₂ uptake and release, or possible contamination in the H₂ stream. Inset: Structure of Zn₂(bpdcc)₂(bpee) along axis showing 1-dimensional pores.

to a much higher uptake than expected for the metal alone. To date, hydrogen storage reports for spillover systems suggest moderate temperature adsorption (i.e. 300 K) and hydrogen uptake approaching DOE goals at 298 K and 100 bar. The highest uptake reported for spillover materials has utilized microporous MMOFs as the receptor for spilled over hydrogen. It is anticipated that optimization of the MMOF structure, surface chemistry, and porosity will further increase this uptake. It is further expected that direct incorporation of metals into the MOF structure will increase surface coverage associated with hydrogen spillover. Our project thus synthesizes new MMOF structures with systematic variation in surface chemistry and porosity to fundamentally explore these factors on the hydrogen spillover process, in order to ultimately optimize the MMOF structure for hydrogen spillover. Further, we will explore direct incorporation of catalytic sites into the MMOF structure to optimize the hydrogen spillover process. We will also fundamentally explore pressure-induced MMOF structural changes in order to incorporate this phenomenon into hydrogen trapping, via both physisorption and hydrogen spillover.

Accomplishments

- Synthesis of four series of new MMOFs using linker and pillar molecules of various length, shape and hydrogen affinity in order to vary pore size, topology, and internal surface. Identification of MMOF structure by these MMOFs was described in the first quarterly report for 2009, and included powder X-ray diffraction patterns, selected pore characteristics, and preliminary low temperature H_2 adsorption data to determine isosteric heats of adsorption. Incorporation of Li^+ metal centers into the $(hfpbb)(H_2hfpbb)_{0.5}$ structure. Measurement of isosteric heats of hydrogen (currently ranging from 5-13 kJ/mol) will be useful for comparison of spillover samples based on these MMOFs.
- Validation of RU (1.25 wt%) and PSU (1.25 wt%) hydrogen storage measurements for $Zn_2(bpdC)_2(bpee)$ at 77 K and pressures up to 20 bar on gravimetric equipment (Figure 2).
- Comparison of RU (0.4 wt%) and PSU (0.27 wt%) hydrogen storage measurements at 298 K for the $Cu_3(btc)_2(H_2O)_3$ sample at 300 K and 20 bar (See Figure 3).
- Upgrade of laboratory to include high-purity H_2 delivery system and mass spectrometer for validation of H_2 purity and H_2 desorption. Development of H_2 temperature programmed desorption methods.
- Prediction of gate-opening pressure for Cu-dhbc-bpy of 86 atm [2] based on treatment with statistical mechanics. Analysis of width of hysteresis loop

FIGURE 3. Room temperature (298 K) H_2 adsorption data for $Cu_3(btc)_2(H_2O)_3$: (i) Cycle 1 data obtained gravimetrically at PSU; (ii) Cycle 2 (Repeat Cycle 2 with same sample, equipment, and intermittent pretreatment without air exposure); (iii) mixed 9:1 with 5% PtAC; (iv) sputtered with Pt; and (v) Cycle 1 obtained volumetrically at RU. (inset): View of $Cu_3(btc)_2(H_2O)_3$ structure along the axis of 1-dimensional open channels.

against general predicted behavior for adsorption with substrate relaxation [3].

Future Directions

- The MMOFs to be synthesized during this remainder of 2009 will be designed to vary porosity and surface chemistry.
- Evaluate possible reasons for discrepancies in uptake for $Cu_3(BTC)_2(H_2O)_3$, including differences in pretreatment and sample transfer.
- The hydrogen capacity of these materials will be measured at 77 and 300 K in order to develop a quantitative relation between these structural variables and hydrogen spillover. Once the correlation is developed, we will look to optimize MMOF uptake in order to meet gravimetric and volumetric targets outlined in Tables 1A and 1B.
- Catalyst Tests: We will finalize methods to dope the various MMOF structures with catalyst for efficient transfer of spilled over hydrogen while minimizing the activation temperature of the catalyst in order to maintain MMOF structural integrity. We will develop methods to assess the hydrogen spillover from catalytic centers directly incorporated into the MMOF structure.
- Once catalyst doping methods are finalized, all MMOFs will be doped with Pt catalyst to determine 300 K uptake and enhancement due to spillover effect.

- Hysteresis Effect and Modeling: Validation of theoretical predictions against our own experimental measurements for both Cu-dhbc-bpy and Zn-bpdc-bpee.

FY 2009 Publications/Presentations

1. A. Lueking, Presentation at 2009 Hydrogen Program Annual Merit Review Meeting, May 20, 2009.
2. “MMOFs for Gas Separation and Hydrogen Storage”, Guangxi Normal University, Guilin, P.R. China, April 13, 2009.
3. Jing Li, “Microporous Metal Organic Frameworks: New Sorbent Materials for Hydrogen Storage”, 4th Conference on Hydrogen Storage Materials, Guangzhou, P.R. China, April 10–12, 2009.
4. A. Lueking, “Novel Nanomaterials for Hydrogen Storage via Hydrogen Spillover and Hydrogen Trapping,” Invited Seminar, Texas A&M University, February 27, 2009.
5. Jing Li, “Porosity and Functionality: Development of MMOFs for Gas Storage and Separation”, University of Leipzig, Leipzig, Germany, October 30, 2008.
6. A. Lueking “Hydrogen Trapping through Designer Hydrogen Spillover Molecules”, DOE Kick-Off Meeting, September 29, 2008.

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IV.D.1a Hydrogen Storage Engineering Center of Excellence (HSECoE)

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Universite du Québec, a Trois-Rivieres, Québec, Canada

Project Start Date: February 1, 2009

Project End Date: January 30, 2014

Objectives

- Develop system models that will lend insight into overall fuel cycle efficiency.
- Compile all relevant materials data for candidate storage media and define future data requirements.
- Develop engineering and design models to further the understanding of on-board storage energy management requirements.
- Develop innovative on-board system concepts for metal hydride, chemical hydride, and adsorption hydride materials-based storage technologies.
- Design components and experimental test fixtures to evaluate the innovative storage devices and subsystem design concepts, validate model predictions, and improve both component design and predictive capability.
- Design, fabricate, test, and decommission the subscale prototype components and systems of each materials-based technology (adsorbents, metal hydrides, and chemical hydrogen storage materials).

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) System Weight and Volume
- (B) System Cost
- (C) Efficiency
- (D) Durability/Operability

(E) Charging/Discharging Rates

(G) Materials of Construction

(H) Balance of Plant Components

(J) Thermal Management

(K) System Life Cycle Assessments

(L) High Pressure Conformality

(P) Lack of Understanding of Hydrogen Physisorption and Chemisorption

(S) By-Product/Spent Material Removal

Technical Targets

This project is directing the work of a diverse team of engineering organizations to design, build and demonstrate prototype hydrogen storage systems for each metal hydride, chemical hydride and hydrogen sorption materials meeting as many of the DOE Technical Targets for hydrogen storage as possible. This project recently started in February of this year, and thus little quantifiable progress has been made towards meeting the DOE 2010 or 2015 Hydrogen Storage Goals. The technical targets of the center are to demonstrate hydrogen storage systems meeting and making progress towards meeting as many of the DOE Hydrogen Storage Technical Targets as possible. This can best be described with the Go/No-Go decisions established for the Center with DOE.

- Phase 1 Go/No-Go decision is to: Provide a system model for each material sub-class (metal hydrides, adsorption, chemical storage) which shows:
 - Four of the DOE 2010 numerical system storage targets met
 - The status of the remaining numerical targets must be at least 40% of the target
- The Phase 2 Go/No-Go decision is to: Provide at least one full scale system design concept (5 kg H₂ stored) where:
 - Six of the DOE 2015 numerical targets are met
 - The status of the remaining numerical targets must be at least 50% of the target

Approach

A team of leading North American national laboratories, universities, and industrial laboratories, each with a high degree of hydrogen storage engineering expertise cultivated through prior DOE, international, and privately sponsored research and development has been assembled to study and analyze the engineering

aspects of condensed phase hydrogen storage as applied to automotive applications. The team is composed of Savannah River National Laboratory (SRNL), Pacific Northwest National Laboratory, Los Alamos National Laboratory, the National Renewable Energy Laboratory, NASA Jet Propulsion Laboratory, United Technologies Research Center, General Motors (GM), Ford, Lincoln Composites, Oregon State University, the University of Quebec at Three-Rivers, BASF and HSM Systems LLC. This diverse group will bring creativity and originality to the Center, especially in the early stages, when innovative concepts must be identified to develop hydrogen storage systems capable of meeting the stringent DOE goals. The technical activities of the Center are divided into six technology areas: Performance Analysis, Integrated Powerplant/Storage System Analysis, Materials Operating Requirements, Transport Phenomena, Enabling Technologies and Subscale Prototype construction, Testing and Evaluation. The organizational structure of the Center is depicted in Figure 1.

SRNL will coordinate and integrate all of the technical activities performed by the partners as well

as those of the three existing materials centers of excellence. This collaboration will result in enabling DOE to transition seamlessly from materials-intensive discovery and analysis to validated and demonstrated subscale hydrogen storage prototype systems. SRNL will manage the interface between the HSECoE and the existing materials centers of excellence or any subsequent DOE sponsored materials development efforts. This will facilitate dialogue of the technical needs and ultimately result in enhanced productivity for all of the centers. Conduits will be established between other working groups that support DOE's hydrogen programs, including Manufacturing R&D, Office of Vehicle Technologies (OVT), Safety Codes and Standards, and the Hydride Reactivity groups.

Accomplishments

As the Center lead, the following accomplishments were achieved:

- Negotiated final Center work scope and Go/No-Go decisions with DOE.

FIGURE 1. Organizational Structure of the Hydrogen Storage Engineering Center of Excellence

- Refinement of partners' roles and responsibilities.
- Established monthly technology area telecons to manage operation of the Center.
- Organized and led the kick-off meeting held in Washington D.C.
- Made two FreedomCAR Hydrogen Storage Tech Team Presentations in Dearborn, MI.
- Organized and led two Center-wide face-to-face meetings in Golden, CO and Arlington, VA.
- Completed and submitted a Safety Plan for the Center.
- Signed intellectual property agreement by all partners for the Center.
- Established public Web site for the center at www.HSECOE.org for the dissemination of data and technical challenges.

A summary of technical accomplishments the individual Technology Areas follows:

Performance Analysis

- Created a vehicle model framework to aid in the development and understanding of hydrogen storage system requirements for light-duty vehicles.
- Assess the base model accuracy by validating model outputs against compressed hydrogen fuel cell vehicles currently in operation.

Integrated Power Plant Storage System Analysis

- Refined structure of integrated system modeling. Developed simplified model of an on-board reversible storage system for inclusion in vehicle level modeling.
- Developed detailed modeling methods. Applied these tools to examine potential improvements in heat exchanger effectiveness.
- Constructed modeling framework for preliminary analysis of membrane separation methods. Compiled materials and impurities of interest.
- Developed compaction design concept which offers greater flexibility in optimization for heat transfer, simple/low-cost manufacturing and good potential for effective mass transport and durability.

Transport Phenomena

- Compiled and distributed a list of data requirements for storage media to the materials operating requirements technology area.
- Metal Hydride System:
 - Developed general model for NaAlH_4 metal hydride-based storage systems and validated model against heat transfer and kinetics data.

- Conducted preliminary optimization studies with metal hydride model.
- Hydrogen Adsorbent System:
 - Began incorporation of adsorbent thermodynamic models into a multidimensional model.

Materials Requirements

- Obtained materials recommendations from the materials Centers of Excellence for consideration in prototype modeling.
- Identified NaAlH_4 , AX-21 and $\text{NH}_3\text{BH}_{3(s)}$ as prototype materials to be used for initial model development and verification and obtained sufficient data for the two former materials.
- Identified $\text{NH}_3\text{BH}_{3(l)}$, AlH_3 , LiAlH_4 , as candidate off-board rechargeable materials, $2\text{LiNH}_2/\text{MgH}_2$ and $\text{LiNH}_2/\text{MgH}_2$ as candidate on-board rechargeable materials and metal-organic framework (MOF)-5 as a candidate adsorbent material and compiling data necessary parametric analysis.

Future Directions

Performance Analysis

- Link models/data to the Greenhouse gases, Regulated Emissions and Energy use in Transportation model.
- Obtain preliminary vehicle requirements results for base scenario.
- Evaluate prime storage system concepts and technologies for their strengths and weaknesses related to forecourt requirements.

Integrated Power Plant Storage System Analysis

- Refine simplified storage system models to include integration with power plant and vehicle level models.
- Construct fuel cell model for baseline level integrated power plant modeling.
- Construct baseline level storage system models and specify requirements.

Transport Phenomena

- Determine envelope of acceptability for metal hydrides and adsorbents utilizing backward calculation from system requirements.
- Develop initial adsorbent system design concepts.
- Develop advanced metal hydride design concepts.
- Develop initial chemical hydride reactor concepts.

Materials Requirements

- Obtain kinetic and materials data from the materials centers of excellence.
- Identify parametric equations specific to each storage material type.
- Perform statistical fits to materials data and pass parametric equations to the Transport Phenomena Technology Area.
- Assess the effects of bed structuring on kinetics.

Enabling Technologies

- Develop response surfaces to American Society of Mechanical Engineers pressure vessel code requirements.
- Assess the viability of membrane purification as well as alternate methods including adsorbents and scrubbers.

IV.D.1b SRNL Technical Work Scope for the Hydrogen Storage Engineering Center of Excellence: Design and Testing of Metal Hydride and Adsorbent Systems

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Subcontractor:
University of Quebec at Trois-Rivieres, Quebec, Canada

Start Date: February 1, 2009
Projected End Date: January 31, 2014

Objectives

The Savannah River National Laboratory (SRNL) and the University of Quebec at Trois-Rivieres (UQTR) will:

- Compile property data for:
 - NaAlH_4 , a metal hydride.
 - AX-21, an adsorbent.
- Collect property data for other select metal hydrides and adsorbents.
 - Compile list of available analytical techniques to support materials property data requirements.
- Develop acceptability envelope for storage media and vessels.
- Develop numerical models to adequately predict storage system behavior for NaAlH_4 and AX-21-based storage systems.
 - Use the models to design optimized storage systems based on NaAlH_4 and AX-21.
- Develop practical and efficient enabling technologies in the areas of hydrogen purification and demonstrate material compatibility for various systems and components for adsorbent and metal hydride storage materials.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section (3.3) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) System Weight and Volume
- (C) Efficiency
- (E) Charging/Discharging Rate

Technical Targets

The goal of the entire Hydrogen Storage Engineering Center of Excellence (HSECoE) is to provide a system model for each material sub-class (metal hydrides, adsorption, chemical storage) which meets the “Technical System Targets: On-Board Hydrogen Storage for Light-Duty Vehicles”, Table 3.3.2 in the DOE Multi-Year Research and Development Plan – April 2009. The end-of-Phase I, Go/No-Go milestone for the entire HSECoE project is that:

1. Four of the DOE 2010 numerical system storage targets are fully met and that
2. The status of the remaining numerical targets must be at least 40% of the target or higher.

For SRNL's specific technical portion of HSECoE, SRNL will:

- Compile thermochemical data.
- Bound media operating characteristics for metal and adsorption hydride material.
- Develop and apply numerical models that couple mass, momentum and energy balances with chemical kinetics and/or isotherms to simulate hydrogen uptake and discharge.
- Identify technology gaps.
- Identify preliminary system designs to achieve DOE 2015 hydrogen storage goals.

Accomplishments

- Compiled and distributed a list of data requirements for storage media.
- Developed general model for NaAlH_4 metal hydride-based storage systems.
 - Validated model against heat transfer and kinetics data.

- Conducted preliminary optimization studies with model.
- Obtained thermodynamic models for AX-21 adsorbent from University of Quebec.
 - Began incorporation of thermodynamic models into a multidimensional model.
- Determined analytical capabilities available within SRNL to support testing for materials properties that are not available in the literature.
- Initiated materials property database for candidate metal hydride storage materials.
- Initiated work on hydrogen purity/quality.

Introduction

SRNL and UQTR will be involved in several critical aspects of the HSECoE. SRNL will focus primarily on metal hydride storage media, and at a secondary level will work to ensure the integration and synergy of adsorbent and chemical hydride systems developed by other team members. SRNL will apply its expertise in modeling dynamic transport phenomena and chemical processes, materials testing, and system modeling to accomplish its objectives in the proposed effort – developing and applying models to identify viable subscale prototype designs, performing design calculations sufficiently accurate for engineering application, and defining the scope and required measurements for experiments with the selected prototypes. Additionally, SRNL will develop technologies to control the purity of hydrogen delivered from the storage systems and will perform analyses and testing to ensure materials compatibility.

UQTR will develop an efficient adsorption model that can be easily implemented but still accurately predict the adsorption characteristics over a range of temperatures. UQTR will extend its current model for hydrogen adsorption on activated carbons to any adsorbent used in the storage system design.

Approach

The project objectives will be carried out in four areas: Transport Phenomena, Hydrogen Purification, Materials Compatibility and Materials Property Database Development. The Transport Phenomena technology area will focus on the processes and components internal to the storage vessel. Models developed within this technology area will be used to downselect and design scaled prototype storage systems for testing. Other efforts by this technology area will include design of test stations and development of test matrices for required data. Data from the prototype

tests will be used to tune and validate the models. The validated models will then be used to predict the performance of full-scale storage systems. Enhancement of storage media performance by optimizing its geometric form and properties will be investigated. The Hydrogen Purification area will address the separation of particulate and gaseous impurities from hydrogen gas discharged from the storage system. The Materials Compatibility area will be responsible for the investigation of the compatibility of the storage media with the materials comprising the vessel wall and components. In addition, to chemical interaction, the technology team will investigate stresses induced by the expansion of storage media during hydrogen uptake. Property data for select metal hydrides will be assimilated by the Materials Property Database area.

Results

SRNL activities for the HSECoE began on February 1, 2009. The main focus was the development of models for use in optimizing storage system designs and performing parametric sensitivity studies for design optimization. Implementation of the models required data for the storage media. SRNL's charter was modeling and design of storage systems based on metal hydride and adsorbent storage media. Based on the availability of data and apparent performance the media selected for use in the first models were TiCl_3 catalyzed NaAlH_4 as the metal hydride media and AX-21 as the adsorbent media. Data compilation for other media will continue.

A prioritized list of data required for modeling all media classes – metal hydrides, chemical hydrides and adsorbents – was issued. Analytical capabilities within SRNL were identified for the measurement of media properties not available in the literature. A preliminary compilation of metal hydride properties for NaAlH_4 and other media was compiled from current databases. A literature review was completed for binders used to pelletize hydrogen storage media.

A general multidimensional model for NaAlH_4 systems, based on the integrated model in [1], was developed and issued to United Technologies Research Center (UTRC), UQTR and Oregon State University (OSU) who will assist with validation and optimization studies. The model was validated against heat transfer and kinetics data and some characterization of thermal contact resistance for heat transfer surfaces was performed. Thermal contact resistance is particularly important because the principal challenge for metal hydride based storage systems is the removal of heat released during hydrogen uptake by the media. The very low thermal conductivity of the media necessitates the use of heat transfer elements in the vessel. Thus far fins have been considered as the primary enhancements to heat removal. However, SRNL and the Microproducts

FIGURE 1. Sensitivity of Temperature during H_2 Uptake to the Number of Coolant and H_2 Injection Tubes

Breakthrough Institute at OSU are investigating novel micro heat exchange systems for this purpose. Optimization studies have been performed that examine the placement, number and dimensions of coolant tubes and fins within the storage vessel, see Figure 1 [2]. For heat removal with fins, preliminary results indicate that fin orientation relative to the axis of coolant tubes within the storage vessel affects the efficiency, in terms of heat removal per mass of the fins.

A thermodynamic model for hydrogen uptake and discharge by AX-21 was provided to SRNL by UQTR [3,4]. Currently both organizations are working to incorporate the thermodynamic model into a multidimensional model for an adsorbent-based storage system.

As part of the Materials Compatibility area, several papers have been identified detailing studies of the stress in containers of expanding hydride materials. Future work will build a computational model of container wall stress due to hydride expansion, using these studies.

Within the Hydrogen Purification area, a literature review of contaminant gettering and membrane separations has been initiated. Draft lists of candidate storage media have been obtained and technical challenges, including delivery of hydrogen at approximately 3 bar to fuel cells and hydrogen purification at the tank/fueling station and the tank/fuel cell interfaces, are being evaluated.

Conclusions and Future Directions

- Continue optimization studies using model for $NaAlH_4$ -based storage vessels.
- Complete development of multidimensional model for AX-21 adsorbent-based storage systems:
 - Validation of models.
 - Parametric studies.

- Optimization of storage system designs.

- Develop acceptability envelope for media and storage vessel as an interactive model that identifies required system and media properties and dimensions required to meet storage system performance requirements.
- Data compilation for other adsorbent and metal hydride media than AX-21 and $NaAlH_4$.

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IV.D.1c Systems Engineering of Chemical Hydride, Pressure Vessel, and Balance of Plant for On-Board Hydrogen Storage

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Project Start Date: February 1, 2009

Project End Date: January 31, 2014

- Demonstrate the performance of economical, compact, lightweight vessels for a hybrid pressurized metal-hydride and adsorbent system, and containment vessel for a chemical hydride system.
- Guide design and technology down-selection, Go/No-Go decision-making, and address vehicle and market impact through cost modeling and manufacturing tradeoff assessments of the three HSECoE prototype storage systems.

Achieving the objectives will enable PNNL, Savannah River National Laboratory (SRNL), and other HSECoE partners to demonstrate on-board hydrogen storage with the potential to meet 2015 DOE technical targets. This technology and design knowledge will be transferred to the participating automotive original equipment manufacturers (OEMs), thus advancing the hydrogen market sector and production of future hydrogen-powered vehicles.

Objectives

PNNL's objectives address some of the critical engineering challenges that currently limit design optimization and commercialization of on-board hydrogen storage systems. Each of these objectives and corresponding tasks have been established to advance the state-of-the-art in design and engineering for chemical hydride storage, pressure/containment vessel construction, and component miniaturization to achieve PNNL, Hydrogen Storage Engineering Center of Excellence (HSECoE), and DOE goals.

- Demonstrate a high level of performance that meets DOE targets for key components (reactor, solids handling, and heat exchanger) of a solid chemical hydrogen storage system.
- Optimized the design of a structured storage bed and system performance through engineering, including establishment of bulk storage media and system kinetics data to aid in design activities.
- Reduce system volume and weight and optimizing system storage capability, fueling, and dehydriding performance through application of microtechnology and associated architectures to the design of high-efficiency heat exchangers and balance-of-plant (BOP) components.
- Mitigate materials incompatibility issues associated with hydrogen embrittlement, corrosion, and permeability through suitable materials selection for vessel materials, heat exchangers, plumbing, and BOP components.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

General to All Storage Approaches:

- (A) System Weight and Volume
- (B) System Cost
- (C) Efficiency
- (D) Durability/Operability
- (E) Charging/Discharging Rates
- (G) Materials of Construction
- (H) Balance of Plant (BOP) Components
- (I) Dispensing Technology
- (J) Thermal Management
- (K) System Life-Cycle Assessments

Off-Board Regenerable Specific:

- (S) By-Product/Spent Material Removal

Technical Targets

The Center activities being conducted at PNNL range from process modeling and component design/engineering to technology application and prototypical

demonstration. The final ultimate goal of the Center is to demonstrate a (100 g) scaled storage system that meets all sixteen of the DOE storage performance targets. No progress toward these technical targets has been made to-date, since the Center is new and just getting underway. Technical work and modeling that will address the Technical Targets was recently initiated in the 3rd quarter of Fiscal Year 2009.

Accomplishments

The Center activities, and by extension PNNL activities, commenced in the 2nd quarter of FY 2009. To-date the Center partners have completed the initial project planning and award contracting. In addition, the Center Technical Areas and Teams have been established. PNNL accomplishments to-date includes:

- Establishment of the Materials Requirements Technical Area, including establishment of liaisons and connections with the Hydrogen Storage Materials Centers of Excellence.
- Down-selection of candidate hydrogen storage materials an initial set of materials to be used for modeling activities. Part of this down-selection process was to initiate data collection on materials. This data collection is currently in-progress.
- Initiation of a sensitivity study on pressure vessel design that includes construction of materials and cost factors.
- Initiation of process flow diagram and model development for a solid chemical hydride storage system.
- Established common modeling approaches and platform for use among Center partners.

Introduction

To-date there has been multiple on-board vehicle-scale hydrogen storage demonstrations, including several studies to examine phenomena and characteristics that impact the engineering of hydrogen storage systems. However, none of these demonstrations have simultaneously met all of the DOE hydrogen storage program goals. Additionally, engineering of new chemical hydride approaches specifically is in its infancy, with ample opportunity to develop novel systems capable of reaching the DOE targets for storage capacity. Toward this goal, PNNL is proposing to contribute to the HSECoE led by SRNL. The goal of this virtual Center and PNNL's role is to develop and demonstrate low-cost, high-performing on-board solid-state hydrogen storage through a fully integrated systems design and engineering approach.

PNNL will target six key objectives to optimize performance characteristics and reduce the size, weight, and cost of a solid-state hydrogen storage system. This will be accomplished through a carefully engineered and integrated design approach, including application of advanced materials (structural and hydrogen storage), use of micro-scale enhancements of heat and mass transfer, better understanding and tailoring of bulk storage media and system kinetics, and assessments of manufacturing and cost impact based on established models/approaches for technology tradeoff studies. PNNL will also serve multiple leadership roles within the HSECoE to help facilitate collaboration across the Center partnership.

Approach

PNNL will actively contribute to the five Technology Areas proposed as part of the HSECoE led by SRNL. The goal of this virtual Center, and PNNL's role, is to develop and demonstrate low-cost, high-performing, on-board solid-state hydrogen storage through a fully integrated systems design and engineering approach. PNNL will focus scope on six technical tasks:

1. Low Volume Storage Systems for Solid Chemical Hydrides
2. Kinetics and Reactor Design and Testing
3. System Miniaturization Using Efficient Microarchitectures
4. Materials Compatibility and Selection
5. Containment and Pressure Vessels Construction
6. Manufacturing and Cost Analysis.

The outcomes from these six technical development tasks will ultimately feed into the overall Center objectives, prototyping and demonstration activities, including design and construction of the solid chemical hydride prototype system and pressurized composite storage tanks for the metal hydride and absorbent systems.

Achieving the objectives will enable PNNL, SRNL, and other HSECoE partners to demonstrate on-board hydrogen storage with the potential to meet 2015 DOE technical targets. This technology and design knowledge will be transferred to the participating automotive OEMs, thus advancing the hydrogen market sector and production of future hydrogen-powered vehicles.

In addition, the Center is structured around six Technical Areas, with leads for each of: Performance, Cost & Energy Analysis; Integrated Power Plant/Storage System Modeling; Materials Requirements; Transport Phenomena; Enabling Technologies; Subscale Prototyping. These Technical Areas and subsequent Technology Teams have been established, with technical

objectives and task planning now complete for each. PNNL is responsible for coordinating the Materials Requirements Technical Area, as well as various Technical Teams within the Center and among all the partners.

Results

The HSECoE kicked off planning and scope refinement discussions among the partners in the 2nd quarter of FY 2009. PNNL initiated technical development activities in the 3rd quarter of FY 2009 and as a result of the short period of time elapsed, no significant or conclusive data has been generated as of yet.

All PNNL tasks have, however, been initiated, and work is underway. The follow is a description of those tasks and objectives of each:

Low Volume Storage Systems for Solid Chemical Hydrides – As part of the Chemical Hydrogen Storage Center of Excellence (CHSCoE) activities, PNNL recently discovered additives for ammonia borane that completely suppress foaming without affecting the hydrogen release chemistry, which solves a problem that has plagued this material system for some time. This is a significant finding because these new fuel formulations allow consideration of engineered monolithic fuel systems that may have effectively no void volume in the fuel tank, presenting a significant advantage over pelletized systems. As part of the work scope PNNL is working toward engineering and demonstration of a monolithic fuel system can be achieved where the fuel is divided into elements that pack with nearly 100% volume efficiency into a fuel tank. This allows the opportunity to employ an elemental volume-exchange fuel management approach, which potentially makes refueling fairly easy as portions of the tank can be refueled based on how much fuel has been used and further increasing volumetric capacity. This is a paradigm shift in chemical hydride system fueling that will require significant engineering efforts to develop a viable and optimized system design. Much of the necessary ancillary technology already exists; PNNL's objective will be to engineer a complete integrated system. Solid chemical hydride storage with non-foaming solid fuel elements, coupled with a volume-exchange approach in the fuel tank, can likely meet the challenging 2015 volumetric capacity target of 0.8 kg/L for a system. It should also meet the gravimetric density target of 9 wt%, with kinetics properties capable of meeting the rate target of $\sim 1.6 \text{ g H}_2/\text{s}$ for an 80 kW fuel cell.

Kinetics and Reactor Design and Testing – Studies on reaction kinetics are valuable when engineering the size of a device that might be used to release hydrogen from solid hydrogen carriers. For example, bench-scale data and proven reactor models for chemical

hydride systems are invaluable when working toward a competent design. PNNL has initiated activities to develop models for a solid chemical hydride system, taking into account geometrical effects of the reactor on combined heat and mass transfer. Bench-scale kinetics measurements obtained from the CHSCoE will be used as input parameters to these three-dimensional reactor models, which will ultimately provide predictions on the hydrogen release rate under varying operating conditions. Test data on small-scale chemical reactors will be used to validate the component models, and the models will be used to assist in the design of larger-scale reactor systems. Component models and process-flow diagrams will be integrated to form system-level models for assessing BOP components. This work will result in new methods for mechanical fuel handling systems to enable the release of hydrogen with efficient thermal management. There is strong potential for microarchitectures to be developed as part of Task 3 to support this activity as well to reduce reactor volume.

System Miniaturization Using Efficient Microarchitectures – Microchannel processing technology uses component architectures consisting of small channels and reaction chambers having a characteristic dimension of 0.1 to 1 millimeter that enable rapid heat and mass transfer. This facilitates process intensification (high processing capacity per unit volume), permitting system volumes that are typically an order of magnitude smaller than conventional technologies. In addition, these same attributes can improve component efficiency and promote rapid transients. Established PNNL microchannel design approaches are being applied to the development of the chemical hydride reactor and integrated heat exchanger systems to achieve the system size and performance objectives. Likewise, PNNL is applying its microchannel modeling and design methodologies to investigate the potential for integration of a heat exchanger inside of a hybrid storage tank for applications in compact, highly efficient metal hydride and adsorbent systems. The results of this task will enable significant advancement in meeting system volumetric targets. The benefit in component miniaturization through the application of microtechnology has been demonstrated by PNNL and others previously; therefore, with proper adaptation of the technology, DOE volumetric targets should be within reach.

Containment and Pressure Vessel Development – There are a number of challenges in designing a contained hydride or adsorbent system, such as simultaneously maximizing volumetric and gravimetric hydrogen storage capacity, effective thermal management during refueling and hydrogen release, and mitigating hydride or adsorbent decrepitation during cycles resulting in degradation of the storage bed integrity and thermal conductivity. The best solution to address these challenges is likely to be one that integrates a structured

storage bed approach and tank construction that can accommodate a wide range of operating conditions. PNNL has initiated activities, in conjunction with HSECoE partners SRNL, United Technologies Research Center, and University of Quebec at Trois-Rivières to integrate the structured bed design they develop as part of their respective tasks for metal hydride and adsorbent storage materials with an appropriately engineered hybrid pressurized storage vessel. The principal technical focus will be to design the vessel to mitigate the major engineering concern of dealing with the volumetric expansion/contraction during hydriding/dehydriding and thermal management.

Manufacturing and Cost Analysis – To support the HSECoE and ensure a holistic down-selection approach to system design and engineering, PNNL has initiated work toward creating a cost model to perform economic and impact assessments of viable manufacturing methods and technology options. This task is focused on the economics of the three prototype on-board hydrogen storage systems and will include modeling and analysis of fuel costs, cost per unit or configuration, component costs, and manufacturing costs. In addition, a manufacturing-cycle analysis is planned for out-year assessments that will be performed together with a value/impact assessment of technology versus the level of objectives accomplished. Successful completion of this task will provide the necessary financial and technology assessment analyses to enable the selection of the best overall hydrogen storage system.

Conclusions and Future Directions

The HSECoE has been established and research activities recently commenced at PNNL, as well as at other Center partner locations. To date the Center partners have completed the initial program planning and award contracting. In addition, the Center Technical Areas and Teams have been established. PNNL is underway in executing the scope of work as defined in previous sections of this report.

Future planned activities include the scope of work as defined in the results section of this report and presented at the DOE Annual Merit Review.

FY 2009 Publications/Presentations

1. Materials Requirements and PNNL Activities in Support of the HSECoE, USCAR Technical Team Review, Washington, D.C., December 11, 2008.
2. 2009 DOE Hydrogen Program Annual Merit Review, Washington, D.C., May 20, 2009, Presentation STP07.

IV.D.1d Advancement of Systems Designs and Key Engineering Technologies for Materials Based Hydrogen Storage

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Contract Number: DE-FC36-09GO19006

Subcontractor:
HSM Systems, Inc., Fredericton, New Brunswick, Canada

Project Start Date: February 1, 2009
Project End Date: January 30, 2014

Objectives

- Collaborate closely with the Hydrogen Storage Engineering Center of Excellence (HSECoE) partners to advance materials-based hydrogen storage system technologies.
- Develop vehicle/power plant/storage system integrated system modeling elements to improve specification of storage system requirements and to predict performance for candidate designs.
- Establish detailed heat and mass transfer modeling and apply to design improved internal heat exchange configurations.
- Design and evaluate compacted/structured hydride powder beds including integration into the above heat exchange configurations.
- Assess the viability of on-board purification for various storage material classes and purification approaches.
- Conduct risk assessments during the progression of the phased HSECoE efforts to evaluate concepts regarding the "Environmental Health and Safety" target.

Technical Barriers

This project is concerned with assessing and developing all aspects associated with viability of storage systems and therefore addresses a broad set of technical barriers from the Storage section (3.3.4) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan.

- (A) System Weight and Volume
- (B) System Cost
- (C) Efficiency
- (D) Durability/Operability
- (E) Charging/Discharging Rates
- (G) Materials of Construction
- (H) Balance of Plant (BOP) Components
- (I) Dispensing Technology
- (J) Thermal Management
- (K) System Life-Cycle Assessments

Technical Targets

The goals of this project mirror those of the HSECoE which by the end of the first two-year Phase I seek to define systems configurations which can fully meet four of the DOE 2010 numerical system storage targets as outlined in the Multi-Year Research, Development and Demonstration Plan and partially meet the remaining numerical targets to at least 40% of the target or higher.

Accomplishments

This and other HSECoE projects are in their initial stage, having started nominally in February. Given the close coordination and interdependence of many of the activities, a portion of the efforts to date have involved refinement of the partners' roles and task scopes. Accomplishments of the current project include:

- Refined structure of integrated system modeling. Developed simplified model of an on-board reversible storage system for inclusion in vehicle level modeling.
- Developed detailed modeling methods. Applied these tools to examine potential improvements in heat exchanger effectiveness.
- Constructed modeling framework for preliminary analysis of membrane separation methods. Compiled materials and impurities of interest.

- Developed compaction design concept which offers greater flexibility in optimization for heat transfer, simple/low cost manufacturing and good potential for effective mass transport and durability.

Introduction

Physical storage of hydrogen through compressed gas and cryogenic liquid approaches is well established, but has drawbacks regarding weight, volume, cost and efficiency which motivate the development of alternative, materials-based methods of hydrogen storage. Recent worldwide research efforts for improved storage materials have produced novel candidates and continue in the pursuit of materials with overall viability. While the characteristics of the storage materials are of primary importance, the additional system components required for the materials to function as desired can have a significant impact on the overall performance. Definition, analysis and improvement of such systems components and architectures, both for specific materials and for generalized material classes, are important technical elements to advance in the development of superior methods of hydrogen storage.

Approach

The most significant aspect of the approach is the HSECoE structure through which ten prime organizations will collaborate. The partner activities have been coordinated from the initial planning and continue to be refined. The center is comprised of six technology areas:

- Performance, Cost & Energy Analysis
- Integrated Power Plant/Storage System (IPPSS) Modeling
- Materials Requirements
- Transport Phenomena
- Enabling Technologies
- Subscale Prototyping

UTRC's approach involves a broad set of tasks which leverage prior experience, coordinate with other UTRC projects and extend to new areas of concept development. These activities include:

1. Develop system engineering technical elements to understand vehicle/power plant/storage system integrated performance. Coupled modeling of these higher level system aspects is needed to determine the requirements for storage systems and to predict vehicle performance for candidate designs.
2. Determine the thermal, physical and chemical properties of hydrogen storage and component

materials to support modeling and experimental investigations of heat transfer, mass transfer and durability with a focus on the key material behaviors in other UTRC tasks.

3. Conduct safety risk assessments at various levels of fidelity during the progression of the phased HSECoE efforts in order to pursue the concepts with the greatest potential for complete viability including the "Environmental Health and Safety" target. This will include coordination with the three DOE Material Reactivity projects.
4. Support HSECoE partner development of detailed heat and mass transfer modeling and derive simplified component/system performance models.
5. Assess on-board purification methods for their potential to meet minimum fuel flow requirements with acceptable weight, volume and cost. If successful, this would broaden the number of storage materials that are viable for fuel cell applications.
6. Build upon prior storage system prototype heat exchanger designs and examine enhancements to thermal conductivity, integration with compaction of task 7 and tubing configurations.
7. Design and optimize compacted forms of hydride powder to improve volumetrics, significantly improve safety, increase thermal conductivity and if properly designed, improve hydrogen mass transfer.
8. Address material handling challenges for solid chemical storage through refinement of novel concepts in collaboration with HSECoE partners.
9. Support development of overall system design and fabrication including component integration and assembly procedures, focusing on components developed by UTRC.

Note that several of the above tasks in the approach have close synergy, most notably tasks 2, 4, 6 and 7. The project is divided into three phases with the first covering two years. A Go/No-Go decision at the end of Phase I will guide activities and concepts for deeper evaluation in Phase II.

Results

The framework for integrated vehicle/power plant/storage system modeling was refined. Connections of the more detailed component design modeling to the higher level vehicle modeling are diagrammed in Figure 1. The computational framework Matlab was selected as a common language to bridge across the different levels of modeling.

As part of the connection between the simulation levels, a simplified model for on-board reversible hydride storage system behavior for use in vehicle level studies was developed using results produced from

FIGURE 1. Diagram of Multi-Level HSECoE Modeling

detailed simulations. This simplified model captures the transient effects of heat transfer and the temperature/pressure dependent reaction kinetics, approximating the temperature, pressure and composition fields as being homogeneous (lumped parameters). The kinetics model is taken directly from the detailed COMSOL simulation tool developed by Savannah River National Laboratory (SRNL) with support from UTRC. The transient heat transfer representation was constructed with thermal results from COMSOL simulations of a NaAlH₄-based prototype design developed in a prior DOE contract (DE-FC36-02AL67610).

In order to have a common detailed simulation environment across the center partners, the COMSOL multi-physics package mentioned above was installed at UTRC and verified with three dimensional, single fin models developed by SRNL. Solver methods were modified, resulting in over a 4X reduction in execution time. Figure 2 gives a contour plot of temperature during rehydrogenation for a symmetrical sector of the storage system cross section that is representative of the modeling. Additional configurations were constructed for studying behavior and sensitivities of heat exchanger designs including a two dimensional, axisymmetric model running longitudinally along the tubing. In collaboration with SRNL, concepts to reduce temperature differentials across the hydride bed were

FIGURE 2. Temperature Contour of a Single Fin Sector Model

developed and evaluated, focusing on minimizing the large gradients which inherently occur near the heat exchanger tubing.

Detailed models were developed to study the various rate limiting steps that can occur in thin film metallic hydrogen purification membranes. In addition to performance, cost is a critical target for large scale impact of hydrogen in light-duty vehicles. To give some perspective on cost, a simple model was developed with the results shown in Figure 3. Inputs include one refueling of 5 kg per week over a 10-year life. Thus, in order to achieve a level of less than \$0.50 added cost per kg of refueled hydrogen, the purification subsystem

must have a cost of less than \$100 per square foot of membrane material which can achieve better than 300 standard cubic feet per hour per square foot of hydrogen flux. This effort is being leveraged with a separate DOE project at UTRC aimed at developing low cost, high flux membranes. Additional modeling examining the pressure and temperature dependencies of hydrogen flux were also conducted, supporting the conclusion that on-board purification has the greatest potential for chemical storage materials which can provide higher desorption pressures and temperatures than are likely for on-board reversible materials. From the HSECoE storage material candidates, the initial impurities on which to focus were identified as borazine and ammonia.

Experimental capabilities for conducting well controlled uniaxial compaction at elevated temperatures

FIGURE 3. Added Fuel Cost for On-Board Purification

within a glove box environment have been specified and partially procured/constructed. Concepts for how the compacted forms will be integrated with the heat exchanger configurations have been generated and down-selected. The prime approach involves distributed, low cost conduction enhancement, low loss coupling to the heat exchanger tubing and a relatively simple compaction geometry. Initial experiments will be conducted with NaAlH_4 as a representative ball-milled/catalyzed advanced hydride material.

Conclusions and Future Directions

The initial activities within the HSECoE have established collaborative efforts along a number of technical lines including integrated systems analyses, detailed heat/mass transfer modeling, hydrogen quality/purification and compacted structured forms of powdered storage material. Future efforts in these areas will involve:

- Refinement of simplified storage system models to include integration with power plant and vehicle level models.
- Evaluation of forecourt requirements and communication to relevant hydrogen delivery efforts.
- Through detailed COMSOL modeling, evaluate sensitivities and optimize the conduction enhancement level and distribution for the configuration conceived under the compacted structured bed efforts. Develop response surfaces to American Society of Mechanical Engineers pressure vessel code requirements and include guidance from partner Lincoln Composites when including pressure in the optimizations.
- Continue to assess the viability of membrane purification as well as alternate methods including adsorbents and scrubbers. Any future experiments for on-board purification will focus on borazine and ammonia, and involve premixed gases rather than actual discharged hydrogen.
- Produce planar compacted forms of NaAlH_4 and test for thermal and kinetic performance as well as reduction of adverse reactivity in air and water environments.

IV.D.1e Chemical Hydride Rate Modeling, Validation, and System Demonstration

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Start Date: February 2009
Project End Date: February 2014

Objectives

- Act as the Chemical Hydrogen Storage Center of Excellence (CHSCoE) liaison.
- Develop fuel gauge sensors for solid-state hydrogen storage media.
- Mathematically model the aging characteristics (i.e., shelf-life) of candidate hydrogen storage materials.
- Develop rate models for hydrogen release on candidate chemical hydrides.
- Develop novel strategies for start-up and transient operation with candidate chemical hydrides.
- Identify hydrogen impurities and develop novel impurity mitigation strategies.
- Design, build, and demonstrate a subscale prototype reactor that releases hydrogen using chemical hydrides (technology area lead).

Technical Barriers

This project addresses the following technical barriers from the Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) System Weight and Volume
- (C) Efficiency
- (D) Durability/Operability
- (E) Charging/Discharging Rates
- (F) Codes and Standards

Technical Targets (2015)

- Gravimetric Capacity (3 kWh/kg)
- Volumetric Capacity (2.7 kWh/L)
- H₂ Discharge Rate (minimum full flow rate 0.02 H₂ g/s kW)
- H₂ Purity (99.99 % H₂)
- Start-Up Time to Full Flow (5 s @ 20°C, 15 s @ -20°C)
- Loss of Usable H₂ (0.05 g/hr-kg H₂ stored)

Accomplishments

- Demonstrated hydrogen fuel gauge sensor proof-of-concept.
- Provided chemical hydride empirical rate model for hydrogen release to Savannah River National Laboratory (SRNL).
- Finished setting up equipment to perform experiments on:
 - Shelf-life modeling
 - Impurity testing
- Collaboration onset with the CHSCoE:
 - Engineering data collection
 - Materials transfer for testing

Introduction

This project is a new start (February 2009). Hydrogen storage systems based on chemical hydrides require a chemical reactor to release the hydrogen from the storage media, which is a fundamental difference from the other modes of hydrogen storage, adsorbents and metal hydrides. This hydrogen-release reactor is crucial to the performance of the overall storage system, especially in meeting the DOE targets for hydrogen generation rate, transient operation, and startup times. The reactor must be designed to achieve these targets while meeting the constraints of the overall system volume and weight targets.

One challenge in developing efficient reactor designs is in addressing the wide range of applicable variables, including reactant and product phases (solid, liquid, and gas are all possible): exothermic, endothermic, or autothermal reaction thermodynamics; catalyst effectiveness; selectivity; space-time; and reactor volume. The first objective of the LANL team is to quantify these variables for candidate chemical hydride materials through rate expressions modeled from tightly

controlled, well-defined kinetics experiments free of mass and heat transfer effects. In LANL's Phase 1 work, these rate expressions will be applied in system-level models. In Phase 2, the rate expressions will be used with computation fluid dynamics codes to develop novel and efficient reactor designs in collaboration with other Hydrogen Storage Engineering Center of Excellence (HSECoE) partners.

Kinetics experiments can be used to identify routes to optimize catalyst design, improve reactor efficiency, and reduce weight, volume, and cost. The experiments and the resulting rate models will therefore support achieving the objective of optimizing the reactor for an on-board automotive system. In addition, the engineering team will work with the CHSCE to optimize the catalysts for candidate chemical hydride systems.

LANL will also address the unique requirements of on-board automotive hydrogen storage systems. For example, these systems require fast startup, operation over a wide dynamic range (10:1 turndown or greater), and fast transient response to meet the demands of a drive cycle. The LANL team will develop novel reactor designs and operation strategies to meet these transient demands. In addition, the shelf life and stability of the hydrogen storage media is crucial for an automotive system, especially pertaining to safety and cost. Starting with the kinetics models, the LANL team will develop mathematical models for the aging characteristics of candidate hydrogen storage media (for example, complex metal hydrides or chemical hydrides) subjected to a range of environmental factors. These models can be incorporated into system-level models of performance and cost and also used for the development of accelerated aging protocols necessary for later testing.

Approach

Our approaches in fulfilling the needs and requirements for on-board hydrogen storage within LANL's research scope in the HSECoE will employ efforts in both experimental and modeling fronts. Our approaches are broken down based on our work objectives and they are:

1. **Design and Develop Fuel Gauge Sensors for Solid-State Hydrogen Storage Media:** LANL will employ an inexpensive, simple, and robust methods of using the natural properties of the hydrogen storage media to develop novel fuel gauge sensors.
2. **Mathematically Model the Aging Characteristics of Candidate Hydrogen Storage Materials (for example, complex metal hydrides or chemical hydrides):** In collaboration with the material Centers of Excellence, aging experiments will be performed as a function of temperature (0°C–60°C), pressure (0 psig–5,000 psig), percent relative

humidity (0%–90%), and percent air (0%–100%). Collected data will be regressed into a model for predicting the degradation of stored hydrogen storage media as function of geographic location, diurnal cycles, storage temperature, storage pressure, and storage atmosphere (such as humidity and air).

3. **Develop Rate Models for Hydrogen Release on Candidate Chemical Hydrides Relevance to Technical Objectives:** LANL's approach will be to collaborate with the CHSCE on reactor testing candidate chemical hydrides under tightly controlled experimental conditions (such as temperature and pressure) using LANL's in-house designed and built reactors. Intrinsic rates will be determined over ranges of temperature (25°C–200°C), composition, pressure (0 psig–100 psig), and space-time (0.01 s–10 s). Reactor tests will also be performed to ensure that mass and heat transfer effects are negligible. The sought-after data will include selectivity, conversion, hydrogen yield, and mass balances of all reactants and products.
4. **Develop Novel Strategies for Start-Up and Transient Operation with Candidate Chemical Hydrides:** Exothermic reactions offer the greatest opportunities to meet the DOE technical targets of start time to full flow and transient response by taking advantage of the heat generated upon hydrogen release. The heat required to raise the reactor temperature to that of the desired operating temperature can be obtained on-board without external heat sources by designing novel thermal integration strategies coupled with exothermic hydrogen release reactions. Modeling efforts will be conducted to determine which approach has the largest impact on reducing startup time and transient response; additional decision criteria will include reactor mass, reactor volume, and reactor cost.
5. **Identify Hydrogen Impurities and Develop Novel Impurity Mitigation Strategies Relevance to Technical Objectives:** As materials are down-selected and available, we will produce hydrogen from candidate materials and operate small, 5 cm² single-cell proton exchange membrane (PEM) fuel cells to evaluate the quality of the hydrogen. This task will produce durability data on PEM fuel cell operation using hydrogen generated from hydrogen storage materials. Impurity identification can be accomplished by performing post-characterization studies on the PEM fuel cell, such as cyclic voltammetry, scanning electron microscopy (SEM), transmission electron microscopy, X-ray fluorescence, diffuse reflectance infrared Fourier transform spectroscopy, solid-state nuclear magnetic resonance, and high frequency resistance. LANL has previously demonstrated the catastrophic effects of hydrogen impurities generated from ammonia

borane on PEM fuel cells. Prior to the PEM fuel cell test, the impurities generated from ammonia borane were unknown.

Results

Fuel Gauge Sensor Development

A novel fuel gauge sensor has been demonstrated for a mischmetal hydride. Results indicate that the fuel gauge sensor can detect changes in the hydrogen state-of-charge of the mischmetal hydride.

Mathematically Model the Aging Characteristics of Candidate Hydrogen Storage Materials (for example, complex metal hydrides or chemical hydrides)

Our lab is now equipped and ready to perform the aging experiments needed to model the shelf-lives of candidate hydrogen storage materials.

Develop Rate Models for Hydrogen Release on Candidate Chemical Hydrides Relevance to Technical Objectives

Empirical rate models have been provided to SRNL to begin zeroth order system modeling. Rate models are based on the power-law method and the design equation is for flowing systems.

Identify Hydrogen Impurities and Develop Novel Impurity Mitigation Strategies Relevance to Technical Objectives

Impurities of the dehydrogenation of ammonia borane have been identified as borazine, diborane and ammonia. Quantification of the impurities is in progress. Impurities from the thermal decomposition of ammonia borane have been shown to be catastrophic to fuel cell operation and durability.

Conclusions

- Empirical rate models have been transferred to SRNL to begin modeling.
- Novel fuel gauge sensor demonstrated encouraging results for mischmetal hydrides.
- Quantification of impurities will soon commence.
- Shelf-life experiments are currently underway.

Future Directions

Experimental and Characterization

- Develop preliminary reactor design to begin system modeling and integration.
- Continue shelf-life experiments for shelf-life modeling.
- Quantify hydrogen impurities resulting from chemical hydrogen storage media.
- Continue fuel gauge sensor develop and applicability to other relevant hydrogen storage media.

IV.D.1f Key Technologies, Thermal Management, and Prototype Testing for Advanced Solid-State Hydrogen Storage Systems

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Contract Number: DE-AI01-05EE11105

Subcontractor:
California Institute of Technology, Pasadena, CA

Project Start Date: February, 2009
Project End Date: January, 2014

Objectives

- Develop and apply an understanding of storage system requirements for light-duty vehicles.
- Develop innovative on-board system concepts for materials-based storage technologies.
- Develop and test innovative concepts for storage subsystems and component designs.
- Develop multi-level engineering models to address storage subsystem and fuel cycle.
- Design, fabricate, and test subscale prototypes for each material-based technology.

Technical Barriers

This project addresses the following technical barriers from the Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan (referenced to 2015 targets, as revised 2009):

- (A) System Weight and Volume: 5.5 %wt_{sys}, 55 gH₂/kg_{sys}, 40 gH₂/L_{sys}
- (C) Efficiency: 90% on-board/60% off-board
- (D) Durability/Operability: <1% degradation @ 1,500 cycles, etc.
- (E) Charging/Discharging Rates: 3.3 min fill, 0.02 g/kW-s minimum full flow
- (G) Materials of Construction

- (H) Balance of Plant (BOP) Components
- (I) Dispensing Technology
- (J) Thermal Management

Technical Targets

Regarding the technical barriers addressed by JPL's activities within the Hydrogen Storage Engineering Center of Excellence (HSECoE), the main areas that would be the focus of technical efforts would be the nature of Thermal Management, Balance of Plant Components, and Durability/Operability; the last of these will be evaluated directly by a phased effort of testing and analysis at JPL.

Accomplishments

It should be noted that complete Fiscal Year 2009 funding for HSECoE efforts at JPL was not received/available until September 2009. The immediate impact of this delay was of course the inability to make any progress in earnest for the entirety of the period covered by this report. Any achievements listed in this section have been funded so far via JPL-internal sources and/or accomplished in parallel with other DOE-funded activities at JPL. For example, JPL attended the 2009 Annual Merit Review as a participant in the Metal Hydrides Center of Excellence (MHCoE), a parallel effort, while also providing a poster presentation citing HSECoE progress under this effort.

- HSECoE kick-off meeting held in Washington, D.C. (12/08). Although this meeting and subsequent organizational efforts took place outside the scheduled HSECoE period (start: 2/09), the result was significant, as it allowed a key re-scope of the proposed HSECoE approach. JPL attended this meeting via teleconference.
- Tech Team meeting attended by HSECoE partners in Washington, D.C. (12/08).
- Initial HSECoE face-to-face meeting held in Golden, CO (2/09). During this meeting, considered the "official" start to DOE-funded HSECoE activities, the concept of technology areas/teams/tasks was finely tuned. Important teaming activities were accomplished between JPL and HSECoE partner Oregon State University (OSU) in the area of novel heat-exchange devices; the "thermal devices" technology area was created. JPL's task plan and draft milestones completed for Phase 1; "100-day" scope finalized during face-to-face meeting.

- HSECoE face-to-face meeting held in Arlington, VA, during the DOE Annual Merit Review (6/09).

Introduction

Activities at the JPL under the auspices of DOE's HSECoE have been designed to contribute to the development of advanced automotive solid-state hydrogen storage systems that meet or exceed the DOE/FreedomCAR technical targets for on-board hydrogen storage. JPL performs in several different roles in the HSECoE; the present effort at JPL is divided into several tasks:

- **Advanced Technology Development.** JPL has a lead role in the HSECoE as a Technology Area Lead (TAL) in the area of "Enabling Technologies". This role encompasses the coordination of other partners in the development of technologies for novel thermal devices, fuel sensors, pressure vessels, and gas purity and separation. In addition, JPL has a direct charge under this task of evaluating and developing technologies for passive thermal management for the hydrogen storage system, in both cryogenic and elevated temperature regimes. This role will extend through the entirety of the HSECoE's duration, and involves collaborations with a majority of the HSECoE's partners and a responsibility at the HSECoE Coordinating Council level.
- **Material/Media Evaluation.** As led by Center partner Pacific Northwest National Laboratory (PNNL), JPL will contribute to the evaluation of compatibilities, reactivities, and the engineering properties of candidate metal hydride materials. A subcontract with Caltech will allow assistance with evaluation of hydrogen sorption materials.
- **Thermal Modeling & Validation.** JPL will provide support by preparing and testing thermal hardware as validations of thermal models prepared by other HSECoE partners; this effort will be led by partner Savannah River National Laboratory (SRNL). This testing/validation will be performed at JPL on the "benchmark" and will be in collaboration with other partners.
- **Prototype Concept Engineering.** During the development of the prototype storage system(s) for the various material storage concepts, JPL will provide engineering expertise and oversight in various areas, including but not limited to mechanical design, thermal efficiency, system engineering, control and data acquisition, and materials compatibility. This task will be led by HSECoE partner Los Alamos National Laboratory (LANL).
- **Prototype Testing and Evaluation.** JPL will be responsible for the design, construction, and operation of the test stand used for evaluating the subscale prototype storage system based on metal hydride materials, as well as for the final assembly of the prototype itself. JPL will also acquire, reduce, and analyze the data from the prototype and prepare summary reports. This task is the largest portion of JPL's contribution to the HSECoE, and will be led by LANL.

By means of this breakdown, JPL plans to mix management and direct engineering in a three-phased project of roughly 1.5 years per phase. The nature of technology development implies that much of this effort is being accomplished in an "emergent" manner, allowing for changes to scope, approach, and technology basis. The HSECoE's TAL structure is designed to account for this type of operation.

Approach

JPL's participation in the HSECoE comprises a broad sweep of activities, balanced between technology management on one hand and active research and development on the other. In the latter case, JPL relies on in-house expertise in the areas of thermal engineering, systems design, and hydrogen storage system testing and evaluation. The overall approach involves well-organized and managed communication pathways and closed loops among the other HSECoE partners collaborating with JPL as well as with the HSECoE lead at SRNL. This management approach has a distinctive gestalt derived from the nature of the *Technology Area* concept, wherein key HSECoE partners – including JPL – are responsible for sub-management and direction of agile technical teams, each charged with a particular task in the engineering scope. Figure 1 illustrates this principle. JPL, in this structure, is responsible – via its own work as well as the work of the partner organizations managed within the "Enabling Technologies" technology area – for shepherding the development of key technologies considered necessary for the design and operation of a successful hydrogen storage system.

HSECoE is a widespread effort technically, geographically, and with regard to expertise. JPL maintains a central cognizance within the HSECoE by virtue of its status as a TAL, working closely with HSECoE partners SRNL, LANL, PNNL, and United Technologies Research Center, as well as with OSU, General Motors, Ford, and, via subcontract, Caltech.

FIGURE 1. Graphic representation of the Technology Area concept, showing the flow-down and up-reporting paths as well as hierarchical responsibilities within the HSECoE. In this structure, JPL has cognizance at the Area, Team, and Task level.

Results

As stated above in *Accomplishments*, difficulties with direct funding from DOE have prevented any significant progress during FY 2009. Nevertheless, JPL has been able to accomplish important organizational and management goals, allowing work within the Enabling Technologies TAL to progress, mostly by virtue of the excellent efforts of the HSECoE partners charged with the technical work. In addition, JPL has a vested interest in adding value to HSECoE in order to “make up” for lost time; see *Conclusions* below for specific means by which JPL plans to infuse additional technical accomplishments into future HSECoE efforts.

Conclusions and Future Directions

As currently planned, the HSECoE project will be continuing through early 2014; however, the uncertainty raised by recent Federal budget discussions has led the HSECoE Coordinating Council to discuss an alternate scope for completing work in FY 2009. As a result, much of the planning is centered on creating a “technology footprint”, writing white papers and summarizing the progress of technical and management efforts this far. With this in mind, JPL has considered several near-term goals that will likely be achievable; indeed, now that FY 2009 funding for JPL’s effort is available, rapid progress may be made. There are several broad areas in which JPL plans specific accomplishments:

- JPL efforts on its Thermal Insulation task are now underway; the first steps are to complete initial state-of-the-art assessments and propose approaches to technology gap determination and mitigation.
- During FY 2009, several alternate activities were undertaken at JPL in the area of hydrogen storage system design; these activities ranged from internally-funded research and development “seed” projects to proposal-type designs of working systems. If HSECoE efforts proceed, JPL plans to make efforts to merge its accomplishments in these independent areas into HSECoE as much to gain ground lost during budget downtime as to potentially enhance JPL’s value to both HSECoE and DOE.
- Define communications plan and information flow for “Enabling Technologies” technology area, as compelled by 100-day plan; obtain initial status of collaborating HSECoE partners in charge of sub-teams.
- Determine current status of Systems Improved Numerical Differencing Analyzer modeling/validation effort as originally put “on-hold” during the cessation of engineering “Task E” under the MHCoE, and adopt plan forward for model efforts during HSECoE Phase 2.
- Discuss options for publication, either in refereed journals or direct to DOE for archival purposes, should HSECoE be placed on-hold in FY 2010 due to current Federal budget constraints.

IV.D.1g System Design, Analysis, Modeling, and Media Engineering Properties for Hydrogen Storage

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Project Start Date: February 2, 2009
Project End Date: September 30, 2014

- (E) Charging/Discharging Rates
- (I) Dispensing Technology
- (K) System Life-Cycle Assessments

This project is conducting simulation and modeling studies of advanced onboard solid state hydrogen storage technologies. Insights gained from these studies will be applied toward the design and synthesis of hydrogen storage vessels that meet the following DOE 2015 hydrogen storage for light-duty vehicles targets:

- Cost: \$2/kWh net
- Specific energy: 1.8 kWh/kg
- Energy density: 1.3 kWh/L
- Charging/discharging rates: 3.3 min

Objectives

- Identify optimal pathways for successful hydrogen storage system technologies through modeling, analysis, and testing support.
 - Perform vehicle simulations of various system configurations to support the overall systems engineering technology area.
- Support Savanna River National Laboratory (SRNL) and United Technologies Research Center in defining the fuel interface and forecourt energy requirements.
- Lead tank-to-wheels analyses and provide the Hydrogen Storage Engineering Center of Excellence (HSECoE) with results that will help guide engineering design.
- Compile and obtain media engineering properties for the HSECoE through collaboration with the Hydrogen Storage Materials Centers of Excellence (HSMCoE).

Technical Barriers

This project addresses the following technical barriers from the Storage section (3.3.5) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) System Weight and Volume
- (B) System Cost
- (C) Efficiency

Approach

The work described here is an integral component of DOE's HSECoE and as part of the National Hydrogen Storage Project it will help meet the overall goals of the Hydrogen, Fuel Cells and Infrastructure Technologies Program. DOE's Program supports the Advanced Energy Initiative. NREL's work will support DOE's objectives and expected outcomes of the HSECoE.

The objective of the proposed research is to identify optimal pathways for successful hydrogen storage system technology through modeling, analysis, and testing support. Our first objective will be to perform vehicle simulations of various systems configurations to support the overall systems engineering technology area. The second objective is to support SRNL in defining the fuel interface and forecourt energy requirements. The third objective will be to lead the storage system energy analysis and provide the HSECoE with results that will help guide engineering design. Finally, the fourth objective is to compile and obtain media engineering properties for the HSECoE through collaboration with the HSMCoE.

Accomplishments

In the area of vehicle requirements, NREL has created a vehicle model framework to aid in the development and understanding of hydrogen storage system requirements for light-duty vehicles (Figure 1.). The objective is to take these findings and discover pathways for the successful implementation of hydrogen storage systems that meet DOE performance and cost targets.

FIGURE 1. Hydrogen Storage Vehicle Modeling Evaluation Framework

Hydrogen storage response surfaces specific to a particular hydrogen storage technology are to be integrated with the vehicle model. With the characteristics of each technology embedded within the vehicle model, NREL will be able to analyze vehicle performance as a whole across numerous drive cycles and acceleration tests for each technology. Making trade-offs between various system components and vehicle configurations in the process will help to explore each storage technology's viability in a vehicle system context.

Currently, the tool models hydrogen fuel cell vehicles employing compressed hydrogen storage technologies and includes sensitivity to key powertrain components (e.g. motor, fuel cell, engine, energy storage, hydrogen storage) and all DOE technical targets. NREL has been able to assess the base model accuracy by validating model outputs against compressed hydrogen fuel cell vehicles currently in operation. Specific vehicle parameters of interest were collected for the 2008 Ford Focus FCV, 2008 Honda FCX Clarity and the 2008 Chevrolet Equinox fuel cell vehicle. Published vehicle performance data was also obtained including range, acceleration and fuel economy figures. Each vehicle was modeled with acceleration and fuel economy tests. The model outputs were then compared to the

published data. An error of no more than 6% was observed between published and modeled acceleration performance. Furthermore, the greatest error in combined fuel economy was 2%. The range calculation however yielded a spread in error between 3-30%. It can be speculated that this error is due perhaps to the difference between reporting total hydrogen on-board versus total usable hydrogen on-board.

In cooperation with the integrated power plant/storage system technology team, the compressed hydrogen and fuel models currently serving as place holders will be replaced with detailed fuel cell and storage system response surfaces. These response surfaces will simulate the characteristics for each storage type. This will allow the vehicle model to confirm that the virtual storage system design can provide the hydrogen flow demand within constraints while meeting the imposed targets and vehicle performance goals.

In parallel to the vehicle modeling the NREL team is working on a tank-to-wheel analysis. NREL will be incorporating this analysis into the Greenhouse gases, Regulated Emissions and Energy use in Transportation (GREET) model with fuel and vehicle cycle results to create a total energy-cycle analysis for each hydrogen

storage technology. The vehicle fuel use inputs for this analysis will come from the vehicle performance modeling discussed above. In preparation for the overall life cycle analysis for the center, NREL has coordinated with Argonne National Laboratory and the Storage Systems Analysis Work Group to develop a method for ensuring consistency of assumptions throughout the total well-to-wheels analysis.

Finally, as lead of the DOE Hydrogen Sorption Center of Excellence (HSCoE), NREL is working with our partners and the pertinent scientific community to make sorption material recommendations for future HSCoE materials development efforts and for further analysis by groups assigned by DOE including the HSECoE. NREL identified several materials within four material classes that could meet DOE hydrogen storage system targets. These material classes include: (1) cryocompressed sorbents, (2) substituted materials, (3) multiple hydrogen binding metal centers, and (4) weak chemisorption/spillover. Within each material class, the HSCoE has selected materials for development based on established selection criteria. For each of the selected materials, roadmaps have been constructed to guide development. In addition, NREL has applied selection criteria from the HSECoE to choose a set of materials for further hydrogen storage systems analyses. In the near term, to help calibrate system analysis/design models, the material properties from a standard activated carbon (i.e. AX-21) will be used. However, the HSCoE has identified a short list of materials to begin assembling the requisite properties needed for hydrogen storage system analysis and design. This includes: (a) class 1 cryocompressed materials that have uniform ~1 nm pore sizes that can have very good bulk densities; (b) class 2 BCx materials with high boron concentrations and high surface areas that will enable near ambient temperature storage

temperatures; and (c) class 4 spillover materials that enable ambient temperature storage. Longer term materials development and characterization efforts will be performed as new materials are created with promising hydrogen storage properties. NREL will perform the measurements/characterization needed to provide the HSECoE the requisite material properties for their analysis and design efforts.

Future Directions

- Continue work on system configuration modeling, vehicle simulations, cost analysis, fuel interface requirements, and collaboration with the HSMCoE.
- Identify the hydrogen storage and vehicle applications with the highest value.
- Use experimental investigations and modeling to collect the data necessary to support HSECoE Go/No-Go decisions.
- Work with HSECoE partners to model storage system requirements.
- Work with Pacific Northwest National Laboratory to perform cost analyses.
- Collaborate with HSECoE partners to determine storage system requirements and down-select system design concepts.
- Perform tank-to-wheels analyses and initial energy requirements assessments with HSECoE partners.
- Compile/obtain media engineering properties with HSMCoE.

FY 2009 Publications/Presentations

1. FY 2009 DOE Annual Merit Review Meeting, May 20, 2009, Washington, D.C.

IV.D.1h System Design and Media Structuring for On-Board hydrogen Storage Technologies

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Contract Number: DE-FC36-09GO19003

Project Start Date: March 1, 2009
Project End Date: January 31, 2014

the system design will be optimized with emphasis on meeting following DOE 2010 targets.

Storage Parameter	Units	2010	2015
System gravimetric capacity	(kg H ₂ /kg system)	0.045	0.055
System volumetric capacity	(kg H ₂ /L system)	0.028	0.040
System fill time (for 5 kg H ₂)	min	4.2	3.3
Minimum full flow rate	(g/s)/kW	0.02	0.02
Min-max delivery temperature	°C	-40/85	-40/85

Approach

As part of the Hydrogen Storage Engineering Center of Excellence team, GM has taken up the tasks of building system models for on-board hydrogen storage systems using metal hydrides and adsorbent materials, storage media structuring and enhancement studies, and building a cryoadsorption vessel for validation of cryoadsorption models.

System Modeling: In the first few months, we have concentrated our efforts on adsorbent system simulation modeling. Known adsorbent system materials are generally based on activated carbon or metal-organic frameworks materials. These systems need to be operated at close to liquid nitrogen temperatures and 20-50 bar pressures to provide adsorption capacity necessary for on-board hydrogen storage systems. Therefore, often these systems are also called cryoadsorption systems. For automotive systems, the four cryoadsorption processes occur over different time scales: refueling over a few minutes, discharge over a few hours, dormancy over a few days, and venting over a few weeks. We plan to develop a hierarchy of physics-based models for cryoadsorption hydrogen storage tank to study the relevant engineering issues in these four tank processes. While a lumped parameter model might suffice for the slow processes, we expect significant temperature gradients within the bed for the faster process of refueling, warranting a higher dimensional model. A lumped parameter model for the cryoadsorber tank and a study of the four tank processes has earlier been completed at GM [1].

Storage Media Structuring and Enhancement: To enable fast refueling, it is extremely important to employ storage media with good thermal transport

Objectives

Main objectives of this project are:

- to develop system simulation models for on-board hydrogen storage systems using metal hydride and adsorbent materials and to determine system compliance with the DOE technical targets, and
- to develop storage media structures with optimized engineering properties for use in storage systems.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section of the Hydrogen, Fuel cells and Infrastructure Technologies Program Multi-Year Research, Development, and Demonstration Plan (MYPP):

- (A) System Weight and Volume
- (B) Efficiency
- (C) Charging/Discharging Rates
- (D) Thermal Management

Technical Targets

This project addresses the design of on-board hydrogen storage systems for two types of storage media - adsorbent materials and metal hydrides. In particular,

properties in conjunction with an optimized heat exchanger system to remove the heat generated by the exothermic process of hydrogen uptake. For metal hydrides, another challenge is the fracture of storage media during cycling. Fracturing decreases the heat transfer and enables the increasingly smaller particles to move in the containment vessel and collect at the bottom of the tank with an adverse impact on the system performance. In addition to the potential fracturing of the hydrides, volumetric expansion during hydriding needs to be addressed. By using dimensionally stable media structure and/or a heat exchanger with a pocket design, the negative effects of volumetric expansion can be mitigated. One major objective of this project is to develop, test, and optimize metal hydride composites in the form of pellets or other similar shapes to greatly enhance thermal conductivity of the storage material, to reduce thermal contact resistance and gas flow resistance, and to improve cycling stability and durability of the metal hydride materials. Similarly for adsorbent materials, forming mechanically stable composite pellets out of a powdery material is one promising solution to overcome some of the challenges that we face for on-board hydrogen storage. Pellets or similar-shaped composites of the adsorbent material will be formed using small amounts of binders in combination with thermal enhancing materials. As with metal hydrides, the main objective is to improve thermal conductivity of the storage material, reduce gas flow resistance and to improve cycling stability and durability of adsorbent materials.

Accomplishments

System Modeling: We have selected the lumped parameter model developed earlier at GM [1] to develop system simulation models for the processes in the cryoadsorber tank.

A system simulation schematic for the discharge cycle of a cryoadsorption system is shown in Figure 1. Hydrogen is discharged from the cryoadsorber tank using pressure and temperature control. It is necessary to both raise the tank temperature and reduce pressure to desorb and use most of the hydrogen stored in the tank. Temperature of the system is increased by supplying heat through a heated sidestream of hydrogen. The flow rate and temperature of the sidestream are two control variables that need to be determined through system simulations.

Storage Media Structuring and Enhancement:

We have chosen AX-21 activated carbon as the adsorbent material of choice for media structuring studies. A literature study of various binders used in forming pellets has been completed.

FIGURE 1. A schematic of the cryoadsorption storage system for the discharge cycle. (FC - fuel cell)

Future Directions

- Develop system simulation model for the cryoadsorber system.
- Develop system simulation model for the metal hydride system.
- Conduct simulation studies for both the refueling and discharge cycles for both the metal hydride and adsorbent material systems.
- Test various binders for pelletizing activated carbon and metal hydride materials.
- Measure engineering properties of the pellets for various pellet sizes and optimize composition with respect to engineering properties.

References

1. Senthil Kumar V. et al: A lumped-parameter model for cryo-adsorber hydrogen storage tank, Int. J. Hydrogen Energy 2009; 34: 5466-5475.

FY 2009 Publications/Presentations

1. S. (Darsh) Kumar: Poster Presentation at the 2009 Hydrogen program Annual Merit Review Meeting, stp_12_Kumar.
2. Senthil Kumar V. et al: A lumped-parameter model for cryo-adsorber hydrogen storage tank, Int. J. Hydrogen Energy 2009; 34: 5466-5475.

IV.D.1i Ford/BASF Activities in Support of the Hydrogen Storage Engineering Center of Excellence

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Contract Number: DE-FC36-GO19002

Subcontractor:
BASF, Ludwigshafen, Germany

Project Start Date: February 1, 2009
Project End Date: January 31, 2014

- (C) Efficiency
- (D) Durability/Operability

Technical Targets

This project is conducting vehicle and system level modeling, cost analysis, and materials property assessment/optimization. Insights gained from these studies will be applied towards the engineering of hydrogen storage systems that meet the following DOE 2010 hydrogen storage targets:

- Cost: \$4/kWh net
- Specific energy: 1.5 kWh/kg
- Energy density: 0.9 kWh/L

Approach

As a partner in the Hydrogen Storage Engineering Center of Excellence (HSECoE), Ford will conduct a multi-faceted research project that addresses three of the key engineering challenges associated with the development of materials-based hydrogen storage systems.

First, drawing on our extensive expertise in the engineering of fuel cell (FC) and hydrogen internal combustion engine (H2-ICE) vehicles, we will evaluate and develop system engineering technical elements with a focus on hydrogen storage system operating parameters. This effort will result in a set of dynamic operating parameters and a high-level system model describing the interaction of the fuel storage system with the FC or H2-ICE power plant.

Second, we will leverage the unique capabilities of the “Ford/Massachusetts Institute of Technology cost model” to develop and perform hydrogen storage manufacturing cost analyses for various candidate system configurations and operating strategies. This analysis will facilitate a technology roadmap for potential cost reductions and manufacturing optimization, while providing important feedback to Go/No-Go decisions on prototype design and construction.

Finally, we will evaluate and optimize the “effective engineering properties” of an important class of sorbent materials (MOFs and other framework-like materials) in order to devise improved packing and processing strategies for their use in a systems context. Various mechanical processing routes will be examined (ranging from powders to pelletization to extrusion) in an effort

Objectives

This project will address three of the key technical obstacles associated with development of a viable hydrogen storage system for automobile applications:

- (Task 1) Creation of accurate system models that account for realistic interactions between the fuel system and the vehicle powerplant.
- (Task 2) Development of robust cost projections for various hydrogen storage system configurations.
- (Task 3) Assessment and optimization of the effective engineering properties of framework-based hydrogen storage media (such as metal organic frameworks [MOFs], covalent organic frameworks, etc.).

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) System Weight and Volume
- (B) System Cost

to maximize packing density and heat and mass transfer characteristics.

This work is expected to impact the broader goals for the DOE and FreedomCAR, leading to a significant advance in the engineering of materials-based hydrogen storage systems, refinement in our understanding of the performance targets of hydride materials, and ultimately, the development of commercially-viable hydrogen storage systems.

Accomplishments

The contract for this award was signed on 3/1/2009.

- Participated in the December Center kick-off meeting and the February face-to-face meeting.
- The parameter operating model task (Task 1) was initiated through several teleconference meetings with various project partners. The outcome of the initial modeling discussions was to organize modeling effort into two main technology areas: Performance Analysis and Integrated Power Plant/Storage System Modeling.
- It was determined that the modeling effort by the project partners can best support the HSECoE by providing: (1) confirmation that a virtual H₂ storage system design can operate with a virtual vehicle (i.e. provide hydrogen flow demand within the energy and waste heat budget) and (2) provide H₂ storage system design trade-offs to optimize the performance/targets for a virtual vehicle.
- Reviewed available FC models for waste heat profiles.
- Performed initial comparison analysis of cost estimating approaches and researched the use of a Matlab tool to decompose the H₂ storage system into critical elements for detailed analysis.
- A series of round-robin validation measurements of hydrogen uptake by several candidate framework materials were conducted. These data are summarized in Table 1.

TABLE 1. Round-Robin Validation Measurements of Hydrogen Uptake by Several Candidate Framework Materials

Material	Max. Uptake (wt% H ₂)	Pressure @ Max. (bar)	Sample Mass (g)
Basolite Z377 (MOF-177)	6.9-7.3	~50	0.44
Basolite Z100-H (MOF-5)	5.3-5.6	~45	0.30
Basolite Z200 (IRMOF-8)	3.2-3.3	~20	0.86
Basolite Z1200 (ZIF-8)	2.6-2.7	~15	0.50
Basolite MO50	~0	-	0.77

Future Directions

- The Framework and Power Plant Modeling plans are to identify the common modeling framework and provide partners with the interaction assumptions. The modeling tasks and efforts between the partners at the early stage of the project are important in order for foundational assumptions to be established. Also, the boundary conditions and modeling structures need to be determined.
- Develop the modeling approach and data sources within the hydrogen storage manufacturing cost analysis Technology Team. Identify the role of previous cost analysis (i.e. TIAX) and the methods for handling of sensitive modeling assumptions from either suppliers or original equipment manufacturers.
- Continued characterization of selected framework materials in powdered form. This will include assessing effective volumetric density as a result of powder compaction.

FY 2009 Publications/Presentations

1. Poster presentation at the 2009 Hydrogen Program Annual Merit Review, D. Siegel and M. Veenstra.

IV.D.1j Microscale Enhancement of Heat and Mass Transfer for Hydrogen Energy Storage

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diffusion length associated with that process. As an example, consider a cool fluid flowing in a channel with hot walls. For a diffusion-limited process (laminar flow), the residence time necessary for the fluid to come to the temperature of the walls is a function of channel D^2 where D is the width of the channel. A similar effect is encountered in any other diffusion-limited process. The residence time can be reduced without increasing the pressure drop by adding more channels. If the total flow area is kept constant as the channel dimensions are reduced, moving to a larger number of smaller channels increases heat (or mass) transfer, which in turn allows the channels to be shorter. For laminar flow, the increase in pressure drop caused by reduced channel size is just offset by the impact of the shorter channel on pressure drop. A significant reduction in barriers to heat and mass transfer will improve the heat and mass transfer efficiency and reduce the size, weight, and cost of automotive hydrogen storage systems.

Examples of where OSU has applied microchannel technology to reduce heat and mass transfer barriers include: microscale combustion systems, high flux microscale heat exchangers and recuperators, microtechnology-based heat-actuated heat pumps, microchannel thermal management systems for fuel cells, microscale absorption and adsorption systems, microchannel catalytic reactors for hydrogen production, microchannel biodiesel reactors, microchannel hemodialysis systems, microscale separations systems, and microreactors for the production of nanoparticles. Applying microchannel heat and mass transfer enhancement to diffusion limited energy and chemical systems has often resulted in a reduction factor of 5 to 10 in the size of the device while attaining high thermal and mass transfer efficiency. Currently, four companies are commercializing microtechnology-based energy and chemical systems developed at OSU and the Pacific Northwest National Laboratory (PNNL).

Microscale enhancement of heat and mass transfer can be applied to two classes of problems related to hydrogen storage. First, the microscale enhancement can be used in the actual automotive hydrogen storage component to enhance heat and mass transfer allowing rapid charging of the storage system, rapid startup, and quick response to changing driving conditions. In addition, the overall efficiency of the hydrogen storage system will depend on how efficiently the system can use the available waste heat from the fuel cell. This is particularly true for hydrogen storage systems where material characteristics require temperatures above that available from the fuel cell, mandating the use of

Objectives

Use microchannel technology to:

- Reduce the size and weight of storage.
- Improve charging and discharging rate of storage.
- Reduce size and weight and increase performance of thermal balance-of-plant components.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan (Section 3.3.1):

- (A) System Weight and Volume
- (E) Charging and Discharging Rates
- (H) Balance of Plant (BOP) Components

Technical Targets

Fundamentally, microchannel technology reduces barriers to heat and mass transfer by reducing characteristic diffusion lengths. Any diffusion-limited process can be improved by reducing the characteristic

hydrogen combustion. The performance of the balance-of-plant components, needed for utilization of fuel cell waste heat or combustion of hydrogen, will to a great extent determine the round trip efficiency of the system. The use of microscale components for balance-of-plant applications has the potential to allow efficient use of fuel cell waste heat and efficient combustion of hydrogen for discharging storage. Microtechnology-based balance-of-plant components such as microscale heat exchangers, recuperators, and combustors have been demonstrated for similar applications. Based on OSU's experience in developing other microtechnology-based systems, when compared to conventional components we expect an increase in heat and mass transfer efficiency, and a significant reduction in size and weight.

In the case of metal hydride storage, heat removal during charging is the critical technical issue. Given that the rate limiting processes associated with charging metal hydride storage are typically limited by diffusion, this is a classic example of an application that should be amenable to miniaturization using microchannel architecture. It is currently intended to use waste heat from a high temperature fuel cell to provide heating during discharge. In this case, the role of microscale enhancement would be primarily in enhancing heat removal during charging. Balance-of-plant opportunities will include high performance miniaturized heat exchangers and recuperators. If insufficient waste heat is available from the fuel cell or if a higher discharge temperature is required in the metal hydride storage system, it is straightforward to develop a microtechnology-based integrated hydrogen combustion system with a microchannel combustor and a high effectiveness recuperator to maximize the thermal efficiency of the discharge process.

The first year of the project will identify several high priority applications of microchannel technology to hydrogen storage. At the end of the first year, quantified performance, weight, size and cost goals will be established for each high priority applications.

Approach

The proposed work plan consists of three phases with Go/No-Go decision points at the end of each phase. Working with Savannah River National Laboratory, OSU will develop and supply microchannel-based heat transfer components for both the hydrogen storage component and any balance-of-plant components. In addition, OSU will be available to consult on microchannel-based mass transfer enhancement for the storage system. The goals and objectives are described below:

- **Phase 1: System Requirements & Novel Concepts** – Initially, OSU will focus on system-level simulation conducted by center members to identify and prioritize opportunities for applying microscale heat and mass transfer techniques. Working with other team members, OSU will identify the highest value applications and, where necessary, conduct experimental investigations and use modeling to collect data necessary to support the Go/No-Go decision to proceed to Phase 2. The identification of the specific OSU and PNNL scope of work relative to balance-of-plant components will be defined at the end of year one. Phase 1 will extend from April 1, 2009, to September 30, 2010.
- **Phase 2: Novel Concepts Modeling, Design, and Evaluation** – For each high-priority application, OSU will develop predictive models, design and evaluate components, fabricate proof-of-principle test articles, conduct proof-of-principle tests, and use the results to validate the predictive models. With other team members, OSU will select one or more high-priority components for prototype demonstration. Results will be used to support the Go/No-Go decision to proceed to Phase 3. Phase 2 will extend from October 1, 2010, to September 30, 2012.
- **Phase 3: Subsystem Prototype Construction, Testing, and Evaluation** – For each high-priority component, OSU will design, optimize, and fabricate the component and provide it to the hydrogen storage system integrator. Phase 3 will extend from October 1, 2012, to September 30, 2014.

Accomplishments

This is a new project, funding for this project was available on April 1, 2009, however, we have made significant progress in this limited time period. Key accomplishments are summarized below.

- Worked with other center members we have identified two applications that merit additional investigation. These include:
 - Microtechnology-based energy and chemical systems (MECS)-based structured bed metal-hydride storage where we optimized a unit cell for heat and mass transfer and then “number up” rather than “scale up” using microlamination to produce a full scale hydrogen storage system.
 - Microchannel-based integrated hydrogen combustor/heat exchanger/recuperator plus other balance-of-plant heat exchangers.
- Outlined fabrication strategy for MECS-based metal hydride storage concept.

- Initiated development of the optimization code that will be used to optimize the unit cell for the MECS-based metal hydride storage system.

Future Directions

As indicated above, we are focusing on the development of a MECS-based metal hydride storage concept and an integrated microchannel combustor/heat exchanger. Future research activities are summarized below:

- MECS Metal Hydride Storage Concept
 - Use simulation to optimize unit cell
 - Experimentally validate simulation
 - Outline fabrication approach and production cost
- Integrated Combustor/Heat Exchanger
 - Use simulation to optimize integrated system
 - Fabricate technology demonstration
- Experimentally validate simulation
- Demonstrate rapid start-up and transient performance
- Second Law Analysis
 - Use 2nd Law analysis tools to evaluate thermodynamic losses in hydrogen storage and identify design improvements

Special Recognitions & Awards/Patents Issued

1. One invention disclosure has been filed at OSU.

FY 2009 Publications/Presentations

1. Presentations have been made at the Hydrogen Storage Center of Excellence kick-off meeting and a poster was presented at the 2009 Hydrogen Program Merit Review Meeting.

IV.D.1k Development of Improved Composite Pressure Vessels for Hydrogen Storage

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Contract Number: DE-FC36-09GO19004

Project Start Date: January 1, 2009
Project End Date: December 31, 2013

Objectives

- To improve the performance characteristics, including weight, volumetric efficiency, and cost, of composite pressure vessels used to contain hydrogen in media such as metal hydrides, chemical hydrides, or absorbents.
- To evaluate design, materials, or manufacturing process improvements necessary for containing metal hydrides, chemical hydrides, or absorbents.
- To demonstrate these improvements in prototype systems through fabrication, testing, and evaluation.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) System Weight and Volume
- (B) System Cost
- (G) Materials of Construction

Technical Targets

This project is conducting fundamental studies for the development of improved composite pressure vessels for hydrogen storage. Insights gained from these studies will be applied toward the design and manufacturing of hydrogen storage vessels that meet the following DOE 2010 hydrogen storage targets:

	2010	2015
Gravimetric capacity:	> 6%	> 9%
Volumetric capacity:	> 0.045 kg H ₂ /L	> 0.081 kg H ₂ /L
Storage system cost:	< \$133/kg H ₂	< \$67/kg H ₂

Approach

Lincoln Composites is establishing and documenting a baseline design as a means to compare design, materials and manufacturing processes. This will be used to evaluate potential improvements in design, materials and process to achieve cylinder performance improvements for weight, volume and cost. Lincoln Composites will then down-select the most promising engineering concepts. These will then be evaluated to meet Go/No-Go requirements for moving forward.

Accomplishments

- Finalized design baseline and identified options for improvements in design, materials and processes.
- Identified the following areas for potential evaluation:
 - Evaluation of alternate fiber reinforcement
 - Evaluation of resin toughening agents
 - Evaluation of boss materials and designs
 - Evaluation of damage vs. impact
 - Evaluation of stress rupture characteristics
 - Evaluation of in situ non-destructive examination methods to detect damage
- Conducted testing addressing, specifically, permeation reduction through liner materials. Evaluated polymers with barrier additives and showed a 30-60% reduction in permeation through the liner. Lincoln Composites has also looked into the processing parameters of the liner materials. We evaluated different packing pressures (injection molding) to determine their effect on permeation.

Results showed no significant changes in permeation between the samples. Lincoln Composites has demonstrated testing to saturate and then rapidly depressurize liner samples. Initial testing has shown that with some coatings, blistering forms on the surface of the liner material after depressurization.

Future Directions

- Complete a final report outlining the baseline design.
- Continue to evaluate permeation reduction.
- The evaluation of toughened resin systems will be initiated.
- Stress rupture testing program and cylinder design will be defined and presented to industry members and Hydrogen Storage Engineering Center of Excellence partners for comment.

FY 2009 Publications/Presentations

1. 2009 DOE Hydrogen Program Annual Merit Review, May 20, 2009.

IV.E.1 Analyses of Hydrogen Storage Materials and On-Board Systems

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Contract Number: DE-FG36-04GO14283

Start Date: June 2004

Projected End Date: December 2009

Objectives

The overall objective for this project is provide independent analysis to help guide the DOE and developers toward promising research and development (R&D) and commercialization pathways by evaluating the various on-board hydrogen storage technologies on a consistent basis. Specific objectives include:

- Compare different on-board hydrogen storage approaches in terms of lifecycle costs, energy efficiency and environmental impact;
- Identify and compare other performance aspects that could result in barriers to successful commercialization (e.g., on-board system weight and volume);
- Examine the effects of system-level cost and performance trade-offs for different storage approaches; and
- Project performance and cost relative to DOE targets.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) System Weight and Volume
- (B) System Cost

(K) System Life-Cycle Assessments

Technical Targets

This project evaluates the various on-board hydrogen storage technologies being developed by the DOE Hydrogen Storage Centers of Excellence and independent projects. Insights gained from these evaluations will help guide DOE and developers toward promising hydrogen storage materials and system-level designs and approaches that could meet the DOE targets for storage system cost, specific energy, energy density, fuel cost and efficiency.

Accomplishments

We have performed preliminary and/or updated assessments for several hydrogen storage systems. For each system assessment, we projected on-board system performance and high-volume (~500,000 units/year) manufactured cost, as well as determined the critical cost drivers and conducted single- and multi-variable sensitivity analyses to bound cost results. We also reviewed key assumptions and results with developers, DOE, and stakeholders (e.g., material suppliers, national labs, FreedomCAR and Fuel Partnership Tech Teams) and incorporated their feedback into the final results. Finally, we compared performance and cost results to other baseline technologies and DOE targets for the on-board storage system. Specific accomplishments include:

- Completed liquid hydrogen carrier (LCH₂) system cost assessments based on Argonne National Laboratory's (ANL) performance assessment of Air Products and Chemicals Inc. (APCI) regenerable organic liquid carrier (n-ethylcarbazole-like material¹). The high-volume (500,000 units/yr) on-board system factory cost projection is estimated to be \$15.5/kWh useable hydrogen and the mature market (i.e., 250 tonnes/day [TPD] H₂ eq.) refueling cost projection is estimated to be \$4.74/kg H₂ eq. for the base case assumptions. The on-board system weight and volume estimates are 2.2 wt% and 20 g H₂/L for the base case.
- Updated 5,000 and 10,000 psi compressed hydrogen on-board system factory cost assessments by making slight adjustments to the tank safety factor and carbon fiber requirement

¹ N-ethylcarbazole is toxic and has a low hydrogen storage capacity (i.e., wt%) making it relatively inappropriate for an actual on-board storage media, however it is being used as a representative material for expected carriers to be developed and allows analysis regarding the system, and delivery to be completed.

assumptions to be consistent with ANL's updated analysis and results. The high-volume on-board system factory cost projection is estimated to be \$15.6 and \$23/kWh useable H_2 for 5,000 and 10,000 psi, respectively. The on-board system weight and volume estimates are 5.9 and 4.7 wt%, and 18 and 25 g H_2 /L for 5,000 and 10,000 psi base cases, respectively.

- Completed review of Rohm & Haas (R&H) ammonia borane (AB) regeneration and first fill cost projections based on R&H plant configuration and performance assessments. The mature market (i.e., 100 TPD H_2 eq.) AB regeneration cost projection was estimated to be \$8/kg H_2 eq. and the mature market (i.e., 10,000 TPY AB) AB first-fill cost projection was estimated to be \$9/kg AB.

Introduction

DOE is funding the development of a number of hydrogen storage technologies as part of its "Grand Challenge" applied R&D program. This independent analysis project helps guide the DOE and Grand Challenge participants toward promising R&D and commercialization pathways by evaluating the various hydrogen storage technologies on a consistent basis. Using this consistent and complete comparison of various technology options, R&D can be focused and accelerated. Without such an approach, erroneous investment and commercialization decisions could be made, resulting in wasted effort and risk to the development of hydrogen vehicles and a hydrogen infrastructure.

TIAX is conducting system-level evaluations of the on-board storage systems cost and performance for four broad categories of on-board hydrogen storage. The four categories are: reversible on-board (e.g., metal hydrides and alanates), regenerable off-board (e.g., chemical hydrides), high surface area sorbents (e.g., carbon-based materials), and advanced physical storage (e.g., cryo-compressed hydrogen, liquid hydrogen). Evaluations are based on developers' on-going research, input from DOE and key stakeholders, and in-house expertise.

Approach

This project utilizes an approach that is designed to minimize the risks associated with achieving the project objectives. In coordination with ANL, system-level conceptual designs are developed for each on-board storage system and required fueling infrastructure. We work closely with ANL to develop a bill of materials consistent with their performance assessment. Next, system models and cost models are used to develop

preliminary performance and cost results. We utilize in-house activities and product-based cost models to determine high-volume manufactured cost projections for the on-board storage system, and H₂A-based discounted cash flow models to estimate hydrogen selling prices based on the required off-board hydrogen infrastructure. Subsequently, these results are vetted with developers and key stakeholders and refined based on their feedback. Coordination with DOE's Hydrogen Storage System Analysis Working Group avoids duplication and ensures consistency. This is an on-going and iterative process so that DOE and its contractors can increasingly focus their efforts on the most promising storage technology options.

Results

Our LCH₂ storage system cost projection was estimated based on APCI's liquid hydrocarbon material and a baseline on-board system design developed by ANL [1]. The LCH₂ material hydrogen capacity is assumed to be 5.8 wt%, but the actual useable hydrogen capacity is just 3.7 wt% assuming a 68% storage efficiency (i.e., some hydrogen is burned to supply the heat for dehydrogenation) and a 95% reactor conversion efficiency. Assuming high manufacturing volumes (~500,000 units/year), we estimated the LCH₂ system cost to be approximately \$2,900 for 5.6 kg of useable hydrogen, or \$15.5/kWh (see Figure 1). The reactor catalyst, palladium, accounts for approximately 32% of the overall system cost, and the burner and pumps account for approximately 20% each. We calculated the system's gravimetric and volumetric capacities to be

FIGURE 1. Preliminary On-board Storage System Cost Comparison Results

2.2 wt% and 20 g H₂/L, respectively. The palladium, pumps, media, and burner costs were identified as being key sensitivity parameters, along with the assumed conversion efficiency.

We also conducted a rough on-board system assessment for a hypothetical autothermal liquid carrier media with similar performance assumptions as the baseline LCH₂ media except we assumed a higher material hydrogen storage capacity and usable hydrogen capacity (i.e., hydrogen does not have to be burned on-board to sustain the dehydrogenation reaction). Based on input from APCI, we assumed the hypothetical autothermal carrier offered a hydrogen material capacity of 6.7 wt% (vs 5.8 wt% in the baseline LCH₂ system) and a 100% storage capacity (vs. 68% storage capacity in the baseline LCH₂ system). We further assumed the autothermal system would require an oxidation reactor that uses a V₂O₅ catalyst, but would not require a heat exchange (HEX) burner². The preliminary estimate indicates that the autothermal carrier could offer weight and volume savings of approximately 25-30% over the baseline LCH₂ system, but that cost savings would be minimal (<5%).

In addition to on-board analysis activities, we conducted a preliminary off-board assessment of the LCH₂ system based on performance information obtained from APCI. The off-board analysis includes an estimate of the cost and energy inputs for LCH₂ regeneration, trucking, and vehicle fueling. We examined the scenario in which hydrogen vehicles were filled with LCH₂, and dehydrogenation occurred on-board the vehicle. We developed base case assumptions and cost estimates for the regeneration system based on feedback from APCI. We also analyzed the capacity limitations for hauling LCH₂ and spent material and developed modified H2A Delivery Component models [2] to analyze trucking, reprocessing and fueling station costs. Our preliminary estimate for the hydrogen selling price based on LCH₂ refueling is \$4.7/kg H₂ eq. (see Figure 2). The costs of hydrogen and the liquid carrier are the two dominant factors having the greatest affect on the hydrogen selling price sensitivity. If the LCH₂ is used as an off-board transportation media only (i.e., fueling station dehydrogenation with compressed gas refueling), the hydrogen selling price would increase to approximately \$6/kg.

Next, we updated our baseline on-board cost, weight and volume assessments for the 5,000 psi and 10,000 psi compressed hydrogen (cH₂) storage systems. The assessment included an independent review of the technical performance by ANL [3], comments received from the FreedomCAR & Fuel Partnership Hydrogen Storage Technical Team, input from Quantum, Toray, Structural Composites Inc., and other tank developers/

² Based on feedback from APCI, our rough estimate assumes there would be no net change in cost, weight, and volume resulting from swapping the HEX burner for an oxidation reactor.

FIGURE 2. Preliminary Off-board Refueling Cost Comparison Results

manufacturers via teleconferences. The key change last year included applying the tank safety factor to the nominal tank pressure (i.e., 5,000 and 10,000 psi) rather than maximum filling over pressure (i.e., 6,250 and 12,500 psi) based on new/contradictory information from industry. We also reduced our carbon fiber tensile strength assumption from 2,940 to 2,550 MPa and modified our end dome shape and thickness assumptions to be consistent with the composite pressure vessel algorithm being used by ANL³.

Using these updated assumptions, we estimated the cH₂ system factory costs to be approximately \$2,900 (\$15.6/kWh) for 5,000 psi and \$4,300 (\$23.1/kWh) for 10,000 psi systems storing 5.6 kg of usable hydrogen (see Figure 1). This represents a decrease in cost of 9% for 5,000 psi and 13% for 10,000 psi systems compared to those reported last year. The carbon fiber composite accounts for approximately 70% and 75% of the overall system cost for the 5,000 psi and 10,000 psi tanks, respectively. The range of uncertainty for the tank's carbon fiber purchased cost and safety factor assumptions have the biggest impact on the base case cost estimate (roughly 15-20% each). The updated system gravimetric and volumetric capacities are estimated to be 5.9 wt% and 18 g H₂/L for 5,000 psi and 4.7 wt% and 25 g H₂/L for 10,000 psi systems.

We also evaluated ownership cost (i.e., combination of hydrogen storage system purchased cost and refueling cost) for both the LCH₂ and cH₂ storage systems to compare the combined off-board and on-board costs with other infrastructure options (see Figure 3). Combining the base case on-board system costs (i.e., \$15.4/kWh for LCH₂, \$15.6/kWh for 5,000 psi, and \$23.1/kWh for 10,000 psi), with the projected base case off-board refueling costs (i.e., \$4.74/kg for LCH₂, \$4.21/kg for

³ The resulting pressure vessel design calls for both hoop and helical fiber windings in the cylindrical portion of the vessel, with a 1.8 hoop to helical winding ratio. The end domes consist of only helical windings, and the composite thickness is non-uniform and thickest near the vessel exit hole.

FIGURE 3. Preliminary Fuel System Ownership Cost Comparison Results

5,000 psi, and \$4.32/kg for 10,000 psi) resulted in an ownership costs of roughly \$0.14, \$0.13 and \$0.16 per mile, respectively, based on the assumptions presented in Table 1. The implicit assumption in this ownership cost assessment is that each fuel system and vehicle performs equally well and has the same operating lifetime.

Finally, TIAX completed a high-level review of R&H's cost assessment of the regeneration [4] and first fill production [5] of AB. TIAX reviewed two confidential AB reports generated by R&H in February as well as other relevant reports and evaluated all the process equipment and assumptions in addition to the implementation of these assumptions into the H2A

Delivery Components Model supplied by R&H. Overall, we believe that R&H did an appropriate assessment of the AB first-fill and regeneration costs. The review was partially based on proprietary information received from R&H via the aforementioned reports as well as several conference calls. The AB regeneration pathway was based on a process being evaluated by Los Alamos National Laboratory (LANL).

The estimated baseline AB regeneration cost is projected to be slightly cheaper than the previously analyzed regeneration cost for sodium borohydride (SBH), but more expensive than regeneration cost projection for a liquid hydrocarbon (LCH₂) based on an n-ethylcarbazole-like hydrogen storage media. We expect AB delivery and fueling station costs to be much lower than cH₂ or LH₂ options, but the overall equivalent hydrogen selling price would still likely be more than twice as expensive as these more conventional options. Key cost reduction opportunities include reducing utility and feedstock costs (i.e., electricity, natural gas, hydrogen) which represent over 60% of the regeneration cost. Reducing overall energy use will reduce utility costs as well as improve the primary energy use and greenhouse gas (GHG) emissions results.

R&H calculated the baseline AB first-fill cost to be \$9/kg AB. Approximately 75% of the first-fill cost comes from the cost of SBH, which is assumed to be \$5/kg SBH for the baseline analysis. The first-fill cost has a relatively minor impact on the costs at the regeneration plant (impacting plant storage and material replacement costs),

TABLE 1. Ownership Cost Assumptions

Preliminary Ownership Cost Assumptions	Gasoline ICEV	cH ₂ FCV	cH ₂ FCV	SBH FCV	LCH ₂ FCV	LH ₂ FCV	Basis/Comment
Annual Discount Factor on Capital	15%	15%	15%	15%	15%	15%	Input assumption
Manufacturer + Dealer Markup	1.74	1.74	1.74	1.74	1.74	1.74	Assumed mark-up from factory cost estimates
Annual Mileage (mi/yr)	12,427	12,427	12,427	12,427	12,427	12,427	Car vehicle miles traveled divided by total registrations for 2006
Vehicle Energy Efficiency Ratio	1.0	2.0	2.0	2.0	2.0	2.0	Based on ANL drive-cycle modeling
Fuel Economy (mpgge)	31.0	62.0	62.0	62.0	62.0	62.0	ICEV: Car combined CAFE sales weighted FE estimate for MY 2007
H ₂ Storage Requirement (kg H ₂)	NA	5.6	5.6	5.6	5.6	5.6	Design assumption based on ANL drive-cycle modeling
Fuel Price (\$/eq. gal)	3.00	4.21	4.21	10.14	4.74	4.74	FCV: Equivalent H ₂ price from Off-board Assessment
H ₂ Storage System Factory Cost (\$/kWh)	NA	15.6	15.6	5.0	15.5	14.0	H ₂ storage cost from On-board Assessment

ICEV - internal combustion engine vehicle

FCV - fuel cell vehicle

FE - fuel economy

MY - model year

but it can have a bigger impact on the on-board storage system cost. If we assume the AB hydrogen storage capacity is 16.3 wt%, 34 kg of AB would be required to provide the targeted 5.6 kg H₂ on-board the vehicle, resulting in an on-board storage system cost contribution of approximately \$300 or \$1.60/kWh of stored hydrogen. The DOE 2010 and 2015 cost targets for the complete on-board storage system (inclusive of first-fill, storage tanks, reactors, balance of plant, etc.) are \$4/kWh and \$2/kWh H₂, respectively.

All of the results reported above should be considered in the context of meeting both on-board and off-board cost targets as well as other DOE targets, including on-board system weight, volume, durability/operability, charging/discharging rates; and off-board primary energy use/GHG emissions and fuel purity.

Conclusions and Future Directions

The cost assessments conducted this year allow direct comparison with prior cost assessments and DOE targets. Our models allow us to identify critical cost components, which enables focused discussion with tank developers and manufacturers.

- The base case on-board LCH₂ system evaluated was nearly 4 times more expensive, 2.5 times heavier, and 2 times larger than DOE 2010 targets. The LCH₂ media itself narrowly contains enough hydrogen to meet the DOE on-board system gravimetric target (5.8 wt% vs. 5.5 wt% target). Also, substantial cost reductions and/or performance improvements are needed for the on-board reactor and balance-of-plant (BOP) components to meet targets.
- Although improvements to the LCH₂ material and storage capacities increases system-level weight and volume in the hypothetical autothermal carrier system, they do little to decrease the on-board system cost because the dehydrogenation reactor and BOP account for over 90% of the system cost, and are unaffected by storage capacity. Also, even with the weight and volume improvements, additional material and BOP improvements would be required to meet the 2010 weight and volume targets.
- The off-board LCH₂ hydrogen selling price is approximately 1.6 to 2.4 times the DOE target of \$2-3/kg hydrogen, but is only about 13% more expensive than the 5,000 psi compressed hydrogen delivery option. Additional LCH₂ off-board cost reductions are possible if the carrier material cost is at the low end of the assumed range (\$2-12/gal) or if carrier losses are lower than the assumed 2.75% of media throughput.
- When base case on-board and off-board costs are combined, we see that the LCH₂ fuel system has

potential to have roughly the same ownership cost as a gasoline ICEV when gasoline is assumed to be \$4.25/gal (\$0.14/mile), but 40% higher ownership cost when gasoline is \$3.00/gal⁴.

- The base case 5,000 psi cH₂ system meets the DOE 2010 on-board system gravimetric target, but there is currently no clear path to achieving on-board storage system cost or volume targets as currently configured. The base case 5,000 and 10,000 psi systems evaluated here were 4 and 6 times more expensive, and 2.2 and 1.6 times larger than DOE 2010 targets, respectively. The 10,000 psi system is also 20% above the 2010 target weight.
- When base case on-board and off-board costs are combined, we see that the 5,000 psi cH₂ fuel system has potential to have roughly the same ownership cost as a gasoline ICEV when gasoline is assumed to be \$4.00/gal (\$0.13/mile), but 30% higher ownership cost when gasoline is \$3.00/gal⁴. However, the 10,000 psi fuel system ownership cost will likely be 60% (6¢/mi or ~\$740/yr) higher than a conventional gasoline ICEV for the base case when gasoline is \$3.00/gal.
- An initial AB regeneration cost projection was estimated to be \$8/kg H₂ eq., which is 2.7-4 times more expensive than the total target delivery cost of \$2-3/kg H₂.

The rest of this fiscal year, we plan to continue to work with developers and stakeholders to improve the accuracy of the analyzed on-board and off-board system models to date and evaluate other storage technology options as necessary based on discussions with DOE.

- LCH₂ – update and finalize assumptions and results based on feedback, and complete sensitivity analysis.
- Activated carbon – update and finalize assumptions and results based on updated design and new carbon fiber requirement calculations.
- Cryo-compressed – update based on Lawrence Livermore National Laboratory's Generation 3 Design and new carbon fiber requirement calculations.
- Liquid – incorporate feedback from developers and stakeholders and incorporate relevant updates from the cryo-compressed system assessment.
- New technologies – to be determined by DOE (one or two of the following: AB, adsorbent, alane, MOF177, spillover material, others).
- Update all hydrogen storage systems as necessary to ensure a consistent comparison of storage technologies.

⁴ Different assumptions for annual discount factor, markups, annual mileage and fuel economy would yield slightly different results.

FY 2009 Publications/Presentations

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2. Lasher, S. et al, "Hydrogen Storage Using a Liquid Carrier: On-board System Cost Assessment," Report for Joule Milestone, June, 2008.
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5. Rohm and Haas Company, 2009, "Ammonia Borane Regeneration – LANL Process: Baseline manufacturing Cost Estimate," 1Q 2009 Milestone Report, February 16.

IV.E.2 System Level Analysis of Hydrogen Storage Options

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Start Date: October 1, 2004
Projected End Date: September 30, 2014

Objectives

The overall objective of this effort is to support DOE with independent system level analyses of various H₂ storage approaches, to help to assess and down-select options, and to determine the feasibility of meeting DOE targets. Specific objectives in Fiscal Year 2009 included:

- Model various developmental hydrogen storage systems.
- Provide results to Centers of Excellence (CoEs) for assessment of performance targets and goals.
- Develop models to “reverse-engineer” particular approaches.
- Identify interface issues, opportunities, and data needs for technology development.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) System Weight and Volume
- (B) System Cost
- (C) Efficiency
- (E) Charging/Discharging Rates
- (J) Thermal Management
- (K) System Life Cycle Assessments

Technical Targets

This project is conducting system level analyses to address the DOE 2010 and 2015 technical targets for on-board hydrogen storage systems:

- System gravimetric capacity: 1.5 kWh/kg in 2010, 1.8 kWh/kg in 2015
- System volumetric capacity: 0.9 kWh/L in 2010, 1.3 kWh/L in 2015
- Minimum H₂ delivery pressure: 4 atm in 2010, 3 atm in 2015
- Refueling rate: 1.2 kg/min in 2010, 1.5 kg/min in 2015
- Minimum full flow rate of H₂: 0.02 g/s/kW (2010 and 2015)

Accomplishments

- Analyzed the storage capacity and system performance of the cryo-compressed Gen 3 system with data from Lawrence Livermore National Laboratory.
- Analyzed the gravimetric and volumetric capacities of 5,000- and 10,000-psi compressed hydrogen storage systems and compared them with “Learning Demo” data. Evaluated the overall well-to-tank (WTT) efficiency and greenhouse gas emissions.
- Revised analysis of the storage capacity of the cryogenic activated carbon systems to reflect 2010 and 2015 delivery pressure targets.
- Conducted systems analysis to determine the intrinsic capacities, thermodynamics, dormancy, H₂ refueling dynamics, and discharge dynamics of hydrogen storage in metal-organic framework (MOF) sorbents (MOF-177). Evaluated energy requirement for refueling and discharge.
- Conducted preliminary analysis of lithium alanate regeneration using a scheme developed by the University of Hawaii/University of New Brunswick (UH/UNB). Determined the overall fuel cycle efficiency and greenhouse gas emissions.
- Conducted preliminary analysis of alane regeneration by the electrochemical method using data from Savannah River National Laboratory (SRNL). Determined the overall fuel cycle efficiency and greenhouse gas emissions.
- Performed preliminary energy, efficiency and ammonia borane (AB) regeneration using the process chemistry developed by Pacific Northwest National Laboratory (PNNL). Identified processes that consume significant amounts of energy in

regeneration and provided feedback to Chemical Hydrogen Storage Center of Excellence (CHSCoE).

Introduction

Several different approaches are being pursued to develop on-board hydrogen storage systems with the goal of meeting DOE targets for light-duty vehicular applications. Each approach has unique characteristics, such as the thermal energy and temperature of charge and discharge, kinetics of the physical and chemical process steps involved, and requirements for the materials and energy interfaces between the storage system and the fuel supply system on the one hand, and the fuel user on the other. Other storage system design and operating parameters influence the projected system costs as well. We are developing models to understand the characteristics of storage systems based on these approaches and to evaluate their potential to meet the DOE targets for on-board applications.

Approach

Our approach is to develop thermodynamic, kinetic, and engineering models of the various hydrogen storage systems being developed under DOE sponsorship. We then use these models to identify significant component and performance issues, and to assist DOE and its contractors in evaluating alternative system configurations and design and operating parameters. We establish performance criteria that may be used, for example, in developing storage system cost models. We refine and validate the models as data become available from the various developers. We work with the Hydrogen Storage Systems Analysis Working Group to coordinate our research activities with other DOE analysis projects (such as those of TIAX and the CoEs) to assure consistency and to avoid duplication. An important aspect of our work is to develop overall systems models that include the interfaces between hydrogen production and delivery, hydrogen storage, and the hydrogen user (fuel cell system or internal combustion engine for on-board systems, on-board hydrogen storage subsystem for the off-board systems, etc.).

Results

Hydrogen Storage in Metal-Organic Frameworks

MOFs are considered attractive hydrogen storage materials because of their potential for high intrinsic capacity, ease of production, and on-board reversibility. Of the many MOFs studied to date, MOF-177 has one of the highest hydrogen uptake capacities, 75 g-H₂/kg surface excess at 77 K and 70 bar (110 g/kg absolute) [1].

Figure 1 shows the principal components of the reference on-board hydrogen storage system in which off-board liquid N₂ is used to maintain the MOF-177 at cryogenic temperatures and moderate pressures. We assumed that the sorbent powder is packed inside nominally 2 wt% 40-PPI (pores per inch) Al 2024 foam to compensate for the poor thermal conductivity of MOF-177. An in-tank heat exchanger (9.5 mm internal diameter, 11.9 mm outside diameter u-tubes) removes the heat of adsorption and cools the tank internals during H₂ charging and supplies heat during discharge. The composite pressure vessel consists of T700S carbon fiber (2,550 MPa tensile strength) wound on a 2.4-mm-thick Al 2024 alloy liner, and it is thermally insulated with multi-layer vacuum super insulation ($k = 5.2 \times 10^{-4}$ W/m-K) in a 3-mm-thick Al 2024 alloy vacuum shell. The thickness of the insulation was determined so as to limit the heat transfer rate from the ambient to 2 W. A geodesic winding algorithm was employed to determine the optimal dome shape for the composite vessel and the carbon fiber thickness required for a 2.35 safety factor at the peak storage pressure.

We modeled the MOF-177 hydrogen adsorption isotherms by fitting the low-temperature data of Furukawa et al [1] to the Dubinin-Astakhov equation. We incorporated the fitted isotherms in our system model to estimate the gravimetric and volumetric capacity for 5.6 kg recoverable H₂ at 4-bar minimum delivery pressure and 1.5-kg/min refueling rate. Figure 2 shows the calculated system capacities at 100 K storage temperature with a 50 K temperature swing. At 250 bars, 93% of stored H₂ is recoverable with 24% on MOF and 76% within the void space and pores. The gravimetric capacity peaks at 4.5 wt% at 250 bars and the volumetric capacity peaks at 32.4 kg-H₂/m³ at 450 bars. At 250 bars, the system meets the revised 2010 targets for gravimetric and volumetric capacities. We calculated that the storage medium accounts for 32% of the total system weight and 58% of the total system volume. Nearly 30% of the system weight is due to the containment (liner, carbon fiber and shell) and 27% of the system volume is due to the vacuum insulation and the balance-of-plant components. Our sensitivity analysis shows that the absolute adsorption in MOF-177 needs to be increased by 50% to meet the 2015 targets of 5.5 wt% and 40 kg-H₂/m³ system capacities.

We determined the dormancy capability of the MOF system as a function of the temperature, pressure, and the amount of hydrogen stored at the start of the dormancy period. We estimated the minimum dormancy by analyzing the worst-case scenario in which a MOF tank fully charged with H₂ at 250 bar and 100 K is parked for an extended time. Assuming that the relief valve is set at 25% above the design pressure, H₂ would begin to vent after 15.4 Watt-day of cumulative heat transfer (7.8 days at 2 W heat in-leakage rate). In this

FIGURE 1. Reference MOF-177 On-Board Hydrogen Storage System

FIGURE 2. Usable Gravimetric and Volumetric Capacities of LN_2 -Cooled System

scenario, the calculated peak H_2 loss rate is 0.9 g/h/W and this rate decreases as H_2 vents from the tank.

We determined the amount of liquid N_2 required to satisfy the 1.3 MJ/kg- H_2 on-board and 2.8 MJ/kg- H_2 off-board cryogenic cooling loads. Commercial air

liquefaction units appropriate for service at refueling stations would have a figure of merit of about ~ 0.205 and they would consume ~ 1 kWh of electricity per kilogram of liquid N_2 produced. Thus, the total amount of cryogenic cooling load is ~ 10 kWh/kg- H_2 , which is comparable to the electricity consumed in large central hydrogen liquefaction plants.

In view of the above conclusion, we investigated an alternative system in which the MOF tank is evaporatively cooled by refueling it with liquid H_2 (the adiabatic LH_2 refueling option). In this system, the in-tank heat exchanger is not used during refueling but is still needed during H_2 discharge, but now it can be much more compact since the maximum discharge rate is an order of magnitude lower than the refueling rate. Figure 3 presents the relationship between the storage temperature and the temperature swing that can be sustained with adiabatic refueling with liquid H_2 . There is a minimum temperature that can be established with LH_2 cooling, and although excess adsorption decreases with increase in storage temperature, the recoverable excess is maximum at an intermediate temperature (115 K). Finally, Figure 3 presents the storage

FIGURE 3. Behavior and Performance of System with LH₂ Refueling

temperature (100 K) corresponding to the highest system gravimetric (4.8 wt%) and volumetric (32 kg-H₂/m³) capacities.

Compressed Hydrogen Storage

For reference, we analyzed the gravimetric and volumetric capacities of compressed H₂ tank systems that store 5.6 kg recoverable H₂ at 20-bar minimum pressure (current industrial practice). We considered that the Type IV composite vessel consists of a 5-mm-thick high-density polyethylene liner, carbon fiber (CF), 1-mm glass fiber and 10-mm foam end caps. We determined the optimal dome shape and CF thickness using geodesic and hoop windings along isotenoids with a 2.35 safety factor applied at the nominal design pressure. We calculated that the 5,000-psi system weighs 95 kg and occupies 320 L, yielding 5.9 wt% gravimetric and 17.5 g-H₂/L volumetric capacities. The corresponding 10,000-psi system weighs 119 kg and occupies 222 L, yielding 4.7 wt% gravimetric and 25.2 g-H₂/L volumetric capacities. The CF accounts for 55% and 69% of the total weights for the 5,000-psi and 10,000-psi systems, respectively. We compared our results with data from the “Learning Demonstrations” and found fair agreement for the 10,000-psi system. For the 5,000-psi system, the volumetric capacity data

are similar to our results but the reported gravimetric capacities are considerably lower. We estimated the electrical energy required for compressing and dispensing H₂ for the 20-bar pipeline delivery scenario as 2.9 and 3.7 kWh/kg-H₂ for the 5,000-psi and the 10,000-psi storage option, respectively. The corresponding calculated WTT efficiencies are 57.4% and 55.0%, respectively.

Fuel Cycle Efficiencies of Hydrogen Storage Options Requiring Off-Board Regeneration

We analyzed the off-board regeneration processes for several chemical hydrogen carriers, and determined the energy consumed, the overall fuel cycle efficiency, and life-cycle greenhouse gas emissions.

Ammonia Borane (AB). We constructed and analyzed two engineering flowsheets for regenerating spent AB using the process chemistry developed at PNNL [3]. The flowsheets are based on the concept of achieving high yields by setting up process conditions in which the material to be converted forms the limiting species that is reacted with the other reagents in excess amounts. The process consists of four steps: (1) spent AB digestion by one of two approaches, one that preserves the B-H bonds in the spent AB and the other that recovers the residual H₂ in the spent AB; (2) reduction of the intermediate triphenoxy borane with a metal hydride; (3) formation and recycling of the metal hydride; and (4) addition of NH₃ to form AB. Figure 4 shows the flowsheet for the B-H bond preservation approach. We estimated that the WTT efficiency is 31% without thermal integration and 37% with energy recovery, which can be further improved to 45% if the excess amounts of reagents are reduced. The corresponding WTT efficiencies are 22% without thermal integration and 27% with energy recovery using the second digestion approach. With 30% energy recovery, the weighted CO₂-equivalent greenhouse gas emissions are ~24 kg/kg-H₂ for the B-H bond preservation approach and ~31 kg/kg-H₂ for the H₂ recovery approach to spent AB digestion.

Lithium Alanate. We conducted a preliminary analysis of the UH/UNB process for regenerating LiAlH₄ from LiH, Al, and H₂ in dimethyl ether (DME) solvent at 100 bar and room temperature [4]. We constructed a flowsheet in which DME containing the product LiAlH₄ and excess reactants is recycled without depressurizing the reactor. Our calculations indicate that the energy required for regeneration depends primarily on the molar ratio (α) of DME to LiAlH₄; a lower α reduces energy consumption and increases WTT efficiency. Recent work at UNB has demonstrated regeneration with $\alpha = 5$, for which we calculate a WTT efficiency of 58%. We estimated that α needs to be reduced to 4 to meet the DOE 2010 target of 60% WTT efficiency.

FIGURE 4. Flowsheet for AB Regeneration with Alcohol Digestion [3]

Alane. We analyzed the process for regenerating alane by the electrochemical method, using data obtained at SRNL [5]. In our flowsheet, the starting material is NaAlH_4 , which is formed by reacting spent Al with NaH under moderate H_2 pressure in the presence of Ti catalyst; the NaAlH_4 is then electrolyzed in a tetrahydrofuran (THF) solution to yield alane and NaH. Alane accumulates in the solution as an adduct to THF, $\text{AlH}_3\text{-THF}$, while H_2 evolves at the anode and is consumed at the cathode in a H_2 -neutral net reaction. The solution mixture is withdrawn from the cell, filtered to remove solids (NaH), and pentane is added to precipitate out NaAlH_4 , which is recycled back to the electrochemical cell. Pentane is recovered by distillation at atmospheric pressure and the THF solvent is recovered by two-stage vacuum distillation to maintain the stability of the adduct. Pressure is further reduced to 15 mm Hg to decompose the adduct. Finally, alane is rinsed with pentane and vacuum dried. We calculated that electrolysis and adduct decomposition require significant amounts of electricity and that the WTT efficiency is 26%, which can be improved to ~31% if abundant waste heat at 40°C is readily available to the process.

Conclusions and Future Directions

- Our preliminary analysis indicates that an on-board hydrogen storage system using MOF-177 with LH_2

refueling can achieve ~4.8 wt% usable gravimetric and ~32 g- H_2 /L usable volumetric capacities. A 50% increase in absolute adsorption in MOF-177 is needed to meet the 2015 targets of 5.5 wt% and 40 g- H_2 /L system capacities. A parked vehicle with a fully charged tank (5.6 kg recoverable H_2 stored at 250 bar and 100 K) has 15.4 minimum and 116.4 Watt-day maximum dormancy.

- We have obtained preliminary results for fuel cycle efficiencies of some promising hydrogen carriers that require off-board regeneration. We estimate WTT efficiencies of 31 to 45% for regenerating AB in one of the schemes that uses alcohol to digest and preserve the B-H bond in spent AB. The WTT efficiency is about eight percentage points lower if residual H_2 in spent AB is recovered. Depending on the availability of low-grade waste heat, we estimate a WTT efficiency of 25–31% for regenerating alane by the electrochemical route. We estimate a WTT efficiency of ~58% for regeneration of LiAlH_4 . Reducing the molar ratio of DME to LiAlH_4 by 20% would meet the DOE 2010 target of a WTT efficiency of 60%.
- In FY 2010, we will continue to work with the members of the CHSCoE and Metal Hydride Center of Excellence to analyze alternative off-board methods of regenerating chemical hydrogen carriers. We will also refine our analyses for improved estimates of WTT efficiencies.

- Also in FY 2010, we will extend our systems analysis work to include hydrogen storage in liquid AB.

FY 2009 Publications/Presentations

1. R.K. Ahluwalia and J-K Peng, "Dynamics of Cryogenic Hydrogen Storage in Insulated Pressure Vessels for Automotive Applications," *International J. Hydrogen Energy*, Vol. 33, 4622-4633, 2008.
2. R.K. Ahluwalia, T.Q. Hua and J-K Peng, "Automotive Storage of Hydrogen in Alane," Accepted for publication in *International J. Hydrogen Energy*, 2009.
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4. T.Q. Hua, J-K Peng and R.K. Ahluwalia, "Analysis of Compressed Hydrogen Storage Systems," Storage Systems Analysis Working Group Meeting, Argonne, IL, 26 Feb. 2009.
5. T.Q. Hua and R.K. Ahluwalia, "Preliminary Energy, Efficiency and Greenhouse Gas Analysis of LiAlH_4 Regeneration," Storage Systems Analysis Working Group Meeting, Argonne, IL, 25 Mar. 2009.
6. T.Q. Hua and R.K. Ahluwalia, "Preliminary Analysis of Ammonia Borane Regeneration Using Alcohol Reagent: Energy Consumption, Efficiency and Greenhouse Gas Emissions," Storage Systems Analysis Working Group Meeting, Argonne, IL, 25 Mar. 2009.
7. R.K. Ahluwalia, T.Q. Hua and J-K Peng, "On-board Storage of Hydrogen in Metal Organic Frameworks at Cryogenic Temperatures: The Adiabatic LH2 Refueling Option," Storage Systems Analysis Working Group Meeting, Argonne, IL, 29 Apr. 2009.

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1. H. Furukawa, M. Miller and O. Yaghi, "Independent Verification of the Saturation Hydrogen Uptake in MOF-177 and Establishment of a Benchmark for Hydrogen Adsorption in Metal-Organic Frameworks," *J. Mater. Chem.*, Vol. 17, 3197-3204, 2007.
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IV.E.3 Fundamental Environmental Reactivity Analysis of Hydrogen Storage Materials

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Project Start Date: October 1, 2007
Project End Date: September 30, 2011

Objectives

- Develop internationally recognized standard testing techniques to quantitatively evaluate both materials and systems risks.
- Determine the fundamental thermodynamics and chemical kinetics of the environmental reactivity of hydrogen storage materials.
- Build a predictive capability to determine probable outcomes of hypothetical accident events.
- Develop amelioration methods and systems to mitigate the risks of using these systems to acceptable levels.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan in descending order of impact:

- (F) Codes and Standards
- (P) Understanding of Hydrogen Physisorption and Chemisorption
- (Q) Reproducibility of Performance

Technical Targets

This project is conducting fundamental studies of the air and water exposure of numerous solid state hydride materials in order to assess their risks. Insights

gained from these studies will be applied toward the design of risk mitigation methodologies that meet the following DOE 2010 and 2015 hydrogen storage target:

- Environmental Health and Safety: Meets or exceeds applicable standards.

Accomplishments

- Standardized United Nations (UN) test hazard analyses completed on $2\text{LiBH}_4 \cdot \text{MgH}_2$ and NH_3BH_3 in the fully charged state.
- Water contact completed in charged and discharged states.
- Calorimetric characterization of NH_3BH_3 completed.
- Environmental exposure risk mitigation strategy invention disclosure filed.
- Initial thermal and chemical kinetic model completed having predictive capabilities for environmental exposure and reactivity scenarios.

Introduction

This report gives a summary of standardized UN tests for material packing and shipping, along with calorimetric experiments performed in order to quantify both the rate and the amount of the energy released for hydrogen storage materials. A mathematical modeling effort has been started to predict hydride behavior for hypothesized accidental exposure of the storage materials to an ambient environment, which facilitates an assessment of the risk associated with the utilization of a particular hydrogen storage material. An idealized finite volume model was developed to represent the behavior of dispersed hydride from a breached storage tank or container. Thermodynamic calculations and substantiating calorimetric experiments were performed in order to quantify the energy released, the energy release rates and the reaction products resulting from water and air exposure of ammonia borane. This thermodynamic data will be used in the computational fluid dynamics (CFD) model to predict both the hydrogen generation rates and concentration profiles along with localized temperature distributions. The results of these numerical simulations will be used in future work to predict safety windows and to assist in the design of environmental exposure mitigation strategies.

Approach

In order for the information generated by this project to be widely accepted and globally distributed, an international program was established linking laboratories in North America, Europe and Asia to perform specialized tasks specific to their organizations capabilities. A set of materials testing procedures, based on internationally accepted standards drawn from UN testing procedures has been defined. These tests include exposure to air, humidity, water, and could be modified to include proposed cooling fluids. Numerous potential hydrogen storage materials such as activated carbon, NaAlH_4 , NH_3BH_3 , $\text{LiNH}_2\cdot\text{MgH}_2$, AlH_3 and $2\text{LiBH}_4\cdot\text{MgH}_2$ have been tested identically under these conditions to quantitatively determine their reactivity under normally occurring environmental conditions. Independent studies have been performed to understand the chemical kinetics of these reactions with air, oxygen and water as both liquid and vapor as a function of temperature. Calorimetric studies are continuing to investigate the time-dependent reaction rates of the materials. Mathematical simulations are being developed to predict the behavior of these hydrogen storage materials upon accidental environmental exposure.

Results

UN Tests

The standard materials testing procedures employed are based on existing UN testing protocols that are used to determine the material classification and ensure safe transport and handling [1]. Six standardized tests were performed including (1) water immersion, (2) water

surface contact, (3) water drop testing, (4) pyrophoricity, (5) burn rate, and (6) dangerous self heating. Large amounts of materials were required for some of the tests, in particular the burn-rate and self-heating tests, which presented a challenge in terms of procuring and preparing the material in a standardized state using ball-milling techniques. The UN tests were modified to include visual recording of the testing event, and the addition of thermocouples in those experiments where this was possible.

The first two materials to be evaluated were $2\text{LiBH}_4\cdot\text{MgH}_2$ and NH_3BH_3 . The results of the air and water contact tests have previously been reported for the fully charged state of $2\text{LiBH}_4\cdot\text{MgH}_2$. These tests have been now been completed for NH_3BH_3 , as reported in Table 1.

Calorimeter Experiments

The heat of reaction during dry gas (argon/air) and humid gas (argon/air) exposure was measured for an ammonia borane complex using a gas circulation cell at 40°C and 30% relative humidity for the fully charged and discharged state. The measured heat flow was small and endothermic relative to previous materials tested. The heat flow for ammonia borane in the presence of 30% water vapor for the charged and discharged material under argon and air caused an exothermic reaction to occur. The discharged state has a significantly higher release of heat compared to the charged materials because of the reactivity of the products being formed as the hydrogen is being released and oxidized. The extent of reaction is very slow based on the broadness of the heat flow curves as compared to the previously reported destabilized lithium borohydride and magnesium hydride system.

TABLE 1. Results of the UN Standardized Tests for $2\text{LiBH}_4\cdot\text{MgH}_2$ and NH_3BH_3

Material/ ^{UN} Test	State	Pyrophoricity	Self-Heat	Burn Rate	Water Drop	Surface Contact	Water Immersion
$2\text{LiBH}_4\cdot\text{MgH}_2$	C	No ignition event. Hygroscopic material absorbed H_2O from air.	Self-heated ~300°C within 5 min at $T_{\text{oven}} = 150^\circ\text{C}$ is approached.	Flame propagated in 5 sec with burn rate of 52 mm/sec	2 H_2O drops required for near-instant combustion.	Material combusted	No Ignition event recorded. Gas evolved at longer times. (5 min)
	D	Not tested	Not tested	Not tested	1 H_2O drop required for near-instant ignition	Reaction observed with no flame	Reaction observed with no flame
NH_3BH_3	C	No ignition event. Hygroscopic material absorbed H_2O from air.	Self-heated ~300°C within 10 min, 5 min at $T_{\text{oven}} = 150^\circ\text{C}$	Flame propagate in 6 sec with burn rate of 33 mm/sec	No reactivity detected	No ignition event recorded. Gas evolved at longer times. (5 min)	No reactivity detected
	D	Not tested	Not tested	Not tested	No reaction	No reaction	No reaction

An X-ray diffraction (XRD) examination of the crystalline products was performed of each ammonia borane sample that was exposed to humidified argon and liquid water. In both cases, the XRD of the crystalline products indicated only the presence of ammonia borane. In the case of the liquid water mixing, the expected reaction was $\text{NH}_3\text{BH}_3 + \text{H}_2\text{O} \rightarrow \text{BO}_2^-(\text{a}) + \text{NH}_4^+(\text{a}) + 3\text{H}_2(\text{g})$. From the difference in expected and measured enthalpies (-222 vs 17 kJ/mol), it is more reasonable for the following to be actual reactants, $\text{NH}_3\text{BH}_3 + \text{NH}_3\text{BH}_3 = \text{H}_2\text{O}$.

Numerical Simulations

The numerical simulation examined an environmental exposure of storage material in four different exposure scenarios. In each scenario, the hydride has been released from its containment vessel and formed an axisymmetric pile, making a two-dimensional axisymmetric model appropriate. The governing equations solved for each analysis include mass, momentum, and energy balances. FLUENT, a general purpose CFD package, was used to solve the equations using the finite volume approximation method [2]. In each scenario, a pile of hydrogen storage material in an arbitrary form is exposed to the ambient air, resulting in a chemical reaction that releases hydrogen and heat. However, the location and magnitude of the generation source is different for each scenario. These source locations correspond to hydride falling on a dry surface on a dry day, a wet surface on a dry day, a wet surface on a rainy day and a dry surface on a rainy day. Preliminary heat generation is based on the overall heat of reaction for the production of NaAlH_4 forming from NaH , while the hydrogen mass generation is based on material meeting the DOE 2010 Technical Targets for hydrogen storage [3]. Further details of the mathematical model are available in previous quarterly reports for this project.

For hydrogen ignition, the most important parameters are the upper and lower flammability (UFL, LFL) and explosive limits (UEL, LEL). Another important limit is the autoignition temperature for hydrogen. These limits have been spatially and temporally modeled for the four accident scenarios described above. Hydrogen and heat generation rates hypothetical to simulated results and determine efficacy of the modeling effort and do not represent actual chemical kinetics or thermal discharge rates. Note that each simulation was initialized at 27°C with 0.00% mol fraction of H_2 . Figure 1 presents contour plots of the hydrogen concentration for each scenario after one second. Note that the flammability and explosive limits are marked with solid black lines and that each scenario is marked with a small schematic. Initial results showed that the lower flammability (4%) and lower explosive (17%) limits are reached in less than one second for each

FIGURE 1. Modeling results showing spatial and temporal definition of UFL, LFL, UEL and LEL for hypothetical material ejected from a tank onto the ground after one second under (1) wet surface on a dry day, (2) a dry surface on a wet day, (3) a wet surface on a humid day and (4) a wet surface on a rainy day.

scenario given the constant heat and mass generation sources. In addition, within the pile of material, the upper flammability (75%) and upper explosive (56%) limits are reached in less than one second for Scenarios 1, 3, and 4. The concentration for Scenario 2, which has a top only source at 30% of the maximum generation rate, stays below 35% mol fraction after one second.

Conclusions and Future Directions

Conclusions

1. $2\text{LiBH}_4 \cdot \text{MgH}_2$ in the fully charged state is comparable to NaAlH_4 in risk of ignition during environmental exposure.
2. NH_3BH_3 in the fully charged state poses significantly less risk of ignition than NaAlH_4 during environmental exposure.
3. The mathematical modeling is an effective method of determining heat and hydrogen concentrations developed during simulated accident scenarios.

Future Directions

1. Conduct standardized testing of activated carbon and AlH_3 as decided in consultation with the Centers of Excellence.

2. Continue the thermodynamic and kinetic testing with AlH_3 and $8\text{LiH}:\text{3Mg}(\text{NH}_2)_2$ to feed information into the numerical simulations.
3. Continue modeling effort to include actual chemical kinetics to render predictive capabilities.
4. Evaluate proposed mitigation strategies utilizing calorimetry and modified UN tests.

Special Recognitions, Awards/Patents Issued

This project has been recognized by the International Partnership for the Hydrogen Economy. Partners include the National Institute for Advanced Industrial Science and Technology in Japan, Forschungszentrum Karlsruhe in Germany, Université du Québec à Trois-Rivières in Canada, United Technologies and Sandia National Laboratories in the U.S.

FY 2009 Presentations

1. Fundamental Safety Testing and Analysis of Solid State Hydrogen Storage Materials and Systems, D. Anton, D. Mosher, M. Fichtner, N. Kuriyama, R. Chahine & D. Dedrick, 2nd International Conference on Hydrogen Safety, San Sebastian, Spain, 2008.
2. Solid-State Hydrogen Storage System Development and Engineering Analysis, T. Motyka, D.L. Anton, 2008 ACS/ASM National Meeting on Hydrogen Energy, Cocoa Beach, FL, 2008.
3. The Hydrolysis and Oxidation Behavior of Lithium Borohydride and Magnesium Hydride Determined by Calorimetry, K. Brinkman, J. Gray, B. Hardy, and D. Anton, Materials Research Society (MRS), March 24–28, 2008, San Francisco, California.

4. Environmental Reactivity of Solid State Hydride Materials: Standardized Testing of $2\text{LiBH}_4:\text{MgH}_2$ for Air and Water Exposure, J. Gray, K. Brinkman, B. Hardy, and D. Anton, Materials Research Society (MRS), March 24–28, 2008, San Francisco, California.
5. Environmental Reactivity of the $2\text{LiBH}_4+\text{MgH}_2$ System, D.L. Anton, K. Brinkman & J. Gray, MH2008, Reykjavik, Iceland, June 23–28, 2008.

FY 2009 Publications

1. Fundamental Safety Testing and Analysis of Solid State Hydrogen Storage Materials and Systems, D. Anton, D. Mosher, M. Fichtner, N. Kuriyama, R. Chahine and D. Dedrick, International Journal of Hydrogen Energy, J. Hydrogen Energy, (in press).
2. Design, Fabrication and Testing of NaAlH_4 Based Hydrogen Storage Systems, J. Alloys and Compounds (in press).
3. Hydrogen Storage Properties of Na-Li-Mg-Al-H Complex Hydrides, J. Alloys and Compounds (in press).

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IV.E.4 Quantifying and Addressing the DOE Material Reactivity Requirements with Analysis and Testing of Hydrogen Storage Materials and Systems

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Contract Number: DE-FC36-07GO17032

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Project Start Date: May 15, 2007

Project End Date: May 15, 2010

Objectives

Provide improved definition of the DOE Environmental Health and Safety (EH&S) target and its link to material reactivity to guide research of storage materials. Detailed objectives include:

- Develop qualitative and quantitative analysis tools to evaluate risks for materials-based hydrogen storage systems before and after mitigation methods.
- Perform dust characterization tests for metal hydride, chemical hydride and adsorbent materials.
- Characterize chemical reactions for material exposures associated with both risk events and mitigation approaches using time resolved X-ray diffraction (XRD).
- Assess the trade-offs between residual risk after mitigation and the system weight and volume as well as reaction rates.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies

Program Multi-Year Research, Development and Demonstration Plan [1]:

- (F) Codes and Standards
- (A) System Weight and Volume
- (E) Charging/Discharging Rates

Technical Targets

The key technical target of this project is EH&S, having a focus on the safety sub-target with some consideration for toxicity. The technical target for safety is specified generally as “Meets or exceeds applicable standards.” For metal hydride, chemical hydride and adsorbent materials and systems, however, no such standards exist today. Furthermore, standards currently under development will be high-level in scope, primarily focused on systems and will not provide adequate guidance for evaluating and selecting viable candidate materials. As part of this effort, trade-offs will be evaluated between residual risks after mitigation of the two technical barriers: System Weight and Volume, and Charging/Discharging Rates.

Accomplishments

- Developed customized failure mode and effects analysis (FMEA) for conceptual baseline designs of on-board reversible (using NaAlH_4) and off-board regenerable (using AlH_3) storage systems. Potential safety hazards, failure modes and accident imitators were identified and ranked based on their risk significance.
- Developed and quantified event tree (ET) models for risk-significant accident initiating events identified from FMEA of the on-board reversible storage system.
- Developed fault tree (FT) models for a range of injury categories for blast waves from aluminum dust dispersion. Also, developed FT model for hydride dust dispersion.
- Constructed a framework for economic consequence analysis.
- Identified existing safety Codes & Standards (C&S) (for compressed natural gas [CNG] and compressed hydrogen gas [CHG] applications) that could be modified and credited as hazards control measures in qualitative risk analysis of on-board reversible hydrogen storage systems.
- Performed dust combustion characterization testing of discharged alane powder and Maxsorb activated carbon powder in air and in air-hydrogen

atmospheres. Also, completed testing of partially discharged $2\text{LiBH}_4 + \text{MgH}_2$.

- Designed a rapid depressurization rig to experimentally mimic accidental hydride storage vessel breach and its influence on powder particle size and durability of powder compactions.

Introduction

Safety is one of the most significant issues affecting consumer acceptance and adoption of hydrogen fueled vehicles. Through DOE efforts to understand general public opinions, people have indicated that when selecting a fuel supply, safety is the most important factor. The current project, in close coordination with efforts at Savannah River National Laboratory (SRNL) and Sandia National Laboratories (SNL), will provide quantitative insights to this target and support the development of future risk-informed C&S. The results from these collaborative efforts will also have nearer term impact in guiding storage materials research and the development of materials/systems risk mitigation methods.

Approach

The current project has five distinct elements as follows:

- Risk Analysis:** Formal analysis methods are developed and employed to produce tools which provide increasingly quantitative assessment of the risks associated primarily with on-board vehicle hydrogen storage before and after the use of mitigation methods.
- Standardized Materials Testing:** A set of standard materials tests, focusing on dust explosion, are performed on storage materials to quantify their combustion characteristics under potential risk scenarios and conditions.
- Chemical Reaction Kinetics Testing and Modeling:** Fundamental studies are performed to evaluate the chemical kinetics of material reactions with oxygen, water and various fluids (primarily gases) using time-resolved XRD and other techniques to support the development of risk mitigation methods.
- Risk Mitigation:** Concepts to reduce the consequences of risk-significant failure modes and critical hazards will be devised and investigated both at the material and system levels. The impact on DOE system performance targets will also be determined.
- Prototype System Testing:** This activity was originally planned but unlikely to be pursued given the revised project scope.

Results

During this year (Q4 Fiscal Year 2008 to Q3 FY 2009), the current project accomplished several milestones that are grouped into four categories as follows:

I. Qualitative Risk Analysis (QLRA)

I.1 Developed FMEA for conceptual system configurations of on-board reversible (using NaAlH_4) and off-board regenerable (using AlH_3) storage systems.

I.2 Defined an expert panel for opinion pooling for FMEA of the on-board reversible (using NaAlH_4) system and employed the Delphi process to elicit subject matter experts (SMEs) risk scorings [2]. The panel included SME from DOE, UTRC, SNL, SRNL, automaker original equipment manufacturers, Type-III/Type-IV storage vessel manufacturers, the National Fire Protection Association, University of Maryland Center for Technology Risk Studies, as well as SMEs from Germany, Japan, and Canada. Figure 1 shows the aggregated risk scorings for the top 10 critical hazards/failure modes. The results are based on the first round of SME elicitation using the Delphi iterative process. In this figure, the X-axis represents the identification numbers of the top 10 failure modes [2] of which the top three failure modes are:

- Catastrophic failure of the hydride storage vessel caused by vehicular collision.
- Hydrogen leak caused by pipe rupture in the on-board storage system.
- Hydride storage vessel burst by overpressurization caused by external fire with direct flame impinging upon the storage vessel in conjunction with vessel thermally-activated pressure relief device (TPRD) failure to activate as designed.

In Figure 1, each risk priority number (RPN) is represented by a mean and one standard deviation

FIGURE 1. FMEA/Expert Panel Risk Scorings of the Top 10 Failure Modes

around the mean. The standard deviations reflect the uncertainties of the risk scores assigned by the panel SMEs. It is expected that these uncertainties will decrease in the second round of the Delphi iterative process.

I.3 The major insights of QLRA of the on-board reversible storage system are:

I.3.1 The hydride storage vessel is the most risk significant component in the system, and represents vulnerability of the system to single-point failure should the vessel fail catastrophically. High-severity consequences are associated with scenarios involving catastrophic vessel failure.

I.3.2 The most risk significant accident initiating events (IEs) are: a) vehicular collision leading to hydride vessel rupture, b) external fire leading to vessel burst by overpressurization given failure of vessel TPRD to activate and vent as designed, c) leakage of hydrogen gas from the on-board storage system into a confined (or partially confined) space leading to early or delayed H_2 ignition with possible explosion (deflagration/detonation), and d) water intrusion into the hydride storage vessel leading to in-vessel chemical reaction of the hydride material.

I.4 Crediting Safety Codes and Standards in Qualitative Risk Analysis

Existing as well as newly developed C&S for hydrogen/fuel cell vehicles, such as ANSI/CSA HGV2 [3] and SAE J2579 [4], respectively, are focused on CHG and there is no equivalent C&S for on-board reversible hydrogen storage systems [5]. Part of the current project QLRA included a discussion on the reciprocity between QLRA safety insights and C&S [3]. The discussion demonstrated that structure, system, and component compliance with applicable C&S can be used to support QLRA. Conversely, QLRA insights can support future risk-informed C&S activities related to the on-board storage system. For example, the bonfire test requirements and acceptance criteria in SAE J2579, FMVSS 304 [6] and CSA HGV2, and also the crashworthiness test requirements and acceptance criteria in SAE J2578, SAE J2579, ISO 23273-1 (FCV) and FMVSS 303 can be modified and credited as hazard control measures in FMEA of the on-board reversible hydrogen storage system [5].

II. Quantitative Risk Analysis (QRA)

Three ET models were developed and quantified using the EPRI ETA-II software package. The ET models represented the three risk-dominant

accident initiators: vehicle collision, external fire and hydrogen leakage from the on-board reversible storage system. Figure 2 shows the external fire ET model [5]. The ET top events include hardware failures (e.g., vessel rupture/burst and TPRD failure to vent) and phenomenological events such as hydrogen explosion, hydride chemical reaction with air or water and hydride dust cloud explosion. The ET includes 15 probable accident sequences and associated outcomes (DS-1 through DS-15). The ET also models FMVSS 304 bonfire test acceptance criteria, namely, either the vessel TPRD vents as designed or the vessel survives the fire for 20 minutes [6].

III. Dust Cloud Testing

Dust cloud testing was performed for AX-21 activated carbon, charged and partially-discharged $2LiBH_4 + MgH_2$ and discharged alane. Figure 3 shows the measured pressure rise as a function of time for the materials tested. The largest peak pressure was associated with the discharged alane which is indicative that the metallic form of this material is more reactive than the hydride form. Also for the sample concentration of 250 g/m^3 , $\left(\frac{dP}{dt}\right)$ was the largest of all materials tested to date. The results of dust cloud combustion characterization tests provided useful insights to the probabilistic modeling of dust explosion using fault tree analysis.

IV. Storage Vessel Rapid Depressurization Test

Figure 4 shows the design configuration of a rapid depressurization rig to experimentally mimic accidental hydride storage vessel breach and its influence on powder particle size as well as durability of powder compactions as a risk mitigation method. The key components of the test rig shown in Figure 4 include the hydride powder storage vessel, rupture disk, hydrogen gas supply line, nitrogen purge line, vacuum line and the hydride powder collection vessel.

FIGURE 2. Pressure Profiles of Materials Tested (per ASTM E1226)

IE	TPRD	B	V	H	D	Description	Sequence Path	Seq Frequency
Initiating Event: External Fire	TPRD Vents Vessel(SCA HPRD1 & ISO 23273-2)	No Pressurized Vessel Burst	Vessel Maintains Struct. Integrity	Vented H ₂ Didn't Explode(Un confined)	No Hydride Rx and/or Dust:Cloud Explosion			
IE 2.23E-03	2.22E-05	9.90E-01	2.00E-01	1.00E-01	1.50E-01	DS-1	IE	1.61E-03
						DS-2	IE,H	1.78E-04
						DS-3	IE,V	3.41E-04
						DS-4	IE,V,D	6.02E-05
						DS-5	IE,V,H	3.79E-05
						DS-6	IE,V,H,D	6.69E-06
						DS-7	IE,TPRD	1.98E-10
						DS-8	IE,TPRD,V	2.68E-12
						DS-9	IE,TPRD,V,D	2.65E-10
						DS-10	IE,TPRD,V,H	2.98E-13
						DS-11	IE,TPRD,V,H,D	2.94E-11
						DS-12	IE,TPRD,B	4.42E-10
						DS-13	IE,TPRD,B,D	4.37E-08
						DS-14	IE,TPRD,B,H	4.91E-11
						DS-15	IE,TPRD,B,H,D	4.85E-09

Description of Top Events:

IE = Initiating event: external fire, TPRD = Thermally-activated PRD vents vessel (per CSA HPRD1 & ISO 23272-2), B = No pressurized vessel burst, V = Vessel maintains structural integrity for 20 min (per FMVSS 304), H = Vented H₂ gas didn't explode (*assumption: H₂ vented in an unconfined space*), D = No hydride reaction and/or dust cloud explosion (ASTM and NU tests).

FIGURE 3. External Fire Event Tree Model

FIGURE 4. Storage Vessel Rapid Depressurization Test Rig

Conclusions and Future Directions

The information generated to date included QLRA, QRA and experimental studies. The QLRA included FMEA of two conceptual baseline designs of on-board reversible and off-board regenerable hydrogen storage systems. The QRA covered FT modeling of key phenomena such as hydride dust dispersion, ET modeling of key accident initiating events and framework for economic consequence analysis. The experimental work focused on dust cloud testing of selected hydrogen storage materials.

Future work will focus on:

- I. Continue QLRA efforts by completing design FMEA of the off-board regenerable (using alane) system and analyzing the expert panel's pooled risk scorings for this system.
- II. Continue QRA efforts in three areas: a) ET development and quantification for the remaining dominant accident initiating events, b) economic consequence analysis and assigning monetary safety benefits of selected risk mitigation methods, and c) incorporate results from the experimental and modeling activities at SNL and SRNL into QRA.
- III. Continue experimental efforts in three areas: a) additional dust cloud testing on alane and other materials, b) validation of effectiveness of selected risk mitigation methods, and c) fabrication of the designed rapid depressurization apparatus which mimics hydride storage vessel breach and experimentally investigate the influence of rapid depressurization on powder particle size as well as durability of powder compactions as a risk mitigation method.

FY 2009 Publications/Presentations

1. D.A. Mosher, Y.F. Khalil, X. Tang, B. Laube, and R. Brown, "Quantifying and Addressing the DOE Material Reactivity Requirements with Analysis and Testing of hydrogen Storage Materials & Systems," Technical Team Meeting, USCAR Office, Southfield, MI (April 16, 2009).
2. Y.F. Khalil, D.A. Mosher, X. Tang, B. Laube, and R. Brown, "Quantifying and Addressing the DOE Material Reactivity Requirements with Analysis and Testing of hydrogen Storage Materials & Systems," DOE Hydrogen Program, Annual Merit Review Meeting Arlington, VA (May 18–22, 2009).
3. Y.F. Khalil and D.A. Mosher, "Risk Quantification of Hydride Based Hydrogen Storage Systems for Automotive Applications," 3rd International Conference on hydrogen Safety, Congress Palace, Ajaccio, Corsica, France (September 16–18, 2009).
4. Y.F. Khalil and D.A. Mosher, "Reciprocity of Safety Insights between Risk Analysis and Codes 7 Standards of vehicular hydrogen Storage," Invited Paper at the 2009 Risk Management Conference, Washington, D.C. (November 15–19, 2009).

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IV.E.5 Chemical and Environmental Reactivity Properties of Hydrogen Storage Materials within the Context of Systems

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Project Start Date: July 5, 2007
Project End Date: September 30, 2010

Objectives

- Develop generalized methods and procedures required to quantify the effects of hydrogen storage material contamination in an systems environment:
 - Quantify chemical processes and hazards associated with high and low level contamination of hydrogen storage materials.
 - Predict processes during accident scenarios of systems containing hydrogen storage materials.
 - Identify and demonstrate ex situ and in situ hazard mitigation strategies.
- Provide technical basis for codes and standards (C&S) efforts when appropriate technology maturity has been attained to enable the design, handling and operation of effective hydrogen storage systems for consumer and industrial applications.

Technical Barriers

This project addresses the following technical barriers from the Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) System Weight and Volume
- (D) Durability/Operability
- (F) Codes and Standards
- (Q) Reproducibility of Performance
- (K) System Life-Cycle Assessments

Technical Targets

Technical targets addressed mainly focus on environmental health and safety. This project is enabling the satisfaction of these targets by providing the technical basis for future C&S efforts, thus enabling the design, handling and operation of effective hydrogen storage systems.

Environmental Health & Safety

Toxicity	Meets or exceeds applicable standards
Safety	Meets or exceeds applicable standards

In addition to the above target, other storage technical targets are impacted by this effort as follows:

- Gravimetric and volumetric capacity - This parameter may be influenced by added weight and volume of developed safety systems and mitigation strategies; for example, contamination permeation barriers etc.
- Storage system cost - System cost may be impacted by engineering controls that are developed.
- Fuel purity - Current draft fuel purity standards are based on proton exchange membrane fuel cell requirements. Hydrogen storage materials may have more stringent hydrogen purity requirements.

Accomplishments

Accomplishments can be organized into three focus areas; fundamentals of reactivity, accident scenarios, and hazard mitigation.

Fundamentals of Reactivity

- Reaction conditions resulting in the release of hydrogen from ammonia borane (AB) were identified. Vapor pressures were determined based on isothermal decomposition measurements.
- A bed of AB was exposed to air in the flow-through reactor manifold and was found to be un-reactive up to 103°C.
- Time-lapse images of the decomposition of AB were acquired to help determine the sequence of reactions associated with hydrogen release.
- A chemical kinetics model describing dehydrogenated-alane oxidation processes was developed and a report was distributed to International Partnership for the Hydrogen Economy collaborators.

Accident Scenarios

- We have completed our predictions of processes of a dehydrogenated alan tank at high temperature (150°C) for a variety of simulation variables.
- Model sensitivity studies were performed for the thermal, permeability, and chemical kinetic parameters to determine the confidence levels in breach-in-tank process predictions.
- Permeability models have been developed for a variety of materials including activated carbons, AB, and sodium alanates.
- Data has been acquired for the development of chemical kinetic models for sodium alanate oxidation.

Hazards Mitigation

- We identified a variety of aromatic hydrocarbons as high melting solids for use as non-homogenous reaction and ignition mitigating agents.
- Interactions between sodium alanates and anthracene were investigated through thermal decomposition analysis.
- We have synthesized a new cross-linking monomer with flame-retardant and char-formation properties to be used in microporous scaffolds for metal hydrides.
- Polymerization methods have been developed to encapsulate metal hydrides within a low density polymer scaffold.

Introduction

This project is focused on developing generalized methods and procedures required to quantify the reactivity properties of hydrogen storage materials to enable the design, handling and operation of condensed-phase hydrogen storage systems for consumer and industrial applications. We are performing the experimental and theoretical efforts that are required to understand processes during high-level contamination events including accidents, and low level contamination events experienced during the life cycle of the storage system. This effort provides the technical basis for the identification of hazard mitigation strategies, and eventually development of appropriate codes and standards. The work is organized as following; Task 1 - Quantify chemical processes and hazards during contamination, Task 2 - Predict chemical reactions and hazards during accident scenarios, and Task 3 - Identify and demonstrate hazard mitigation strategies. A successful effort in quantifying the reactivity properties of hydrogen storage materials will enable the safe

design, production, handling, operation, and disposal of consumer and industrial hydrogen storage systems and provide the technical basis for eventual standards developed for safe hydrogen storage systems [1].

Approach

We take a science-based approach to understanding, predicting, and controlling contamination processes of hydrogen storage materials. By first understanding the fundamental contamination reaction processes using a combination of established and newly developed experimental techniques, we are able to build robust and useful chemical kinetic models. These chemical kinetic models are then coupled with heat and mass transfer characteristics to assemble validated models of contamination scenarios. These validated models are then exercised to develop an understanding of the engineering and administrative controls required to mitigate the hazards caused by the contamination processes in the context of systems.

Results

Fundamentals of Reactivity

The reactivity of AB was the focus of the fundamentals of reactivity efforts during Fiscal Year 2009. Qualitatively, AB and its decomposition products are much less sensitive to contamination such as air and water. That being said, AB has other aspects that make it interesting from a reactivity point of view. For example, if the decomposition conditions of AB are not carefully controlled, unfavorable products can be produced, such as diborane and borazine. We are performing experiments on AB that allow us to assess the main features of the reaction network that control the decomposition of AB. By understanding this network, engineers will be able to design systems that optimize the decomposition process and minimize the production of undesirable species that can degrade the reliability of the fuel cell system.

The reaction network of the AB decomposition process is more complex than previous hydrogen storage materials that we have investigated, such as AlH_3 and NaAlH_4 . It involves both gas and condensed phase species and a multi-step process that controls the evolution of hydrogen. We continued our collaboration with the Pacific Northwest National Laboratory (T. Autrey) to perform isothermal decomposition experiments to elucidate reaction processes.

In our experiments, we examined the decomposition of AB under the very lowest and intermediate pressure conditions (see Behrens [2] for more information on the experimental method). Under the lowest pressure conditions, the sample decomposed by the

sublimation of NH_3BH_3 . Under intermediate pressure conditions, the sample decomposes through a more complex reaction pathway than has been described in literature. From our initial experiments at intermediate confinement pressures, it is apparent that a complex nonlinear reaction network controls the evolution of the reaction process. A portion of the results from an experiment that probes the reaction process of AB as it is heated from room temperature to $1,000^\circ\text{C}$ is shown in Figure 1. These data show what occurs in the first stage of the decomposition process. For example, at 90°C the NH_3BH_3 vapor is in equilibrium with the condensed phase AB. About 1,300 seconds after the sample has been held at 90°C , the first H_2 starts to evolve from the sample. Note that the change in the rate of evolution of NH_2BH_2 coincides with that of H_2 . However, closer examination shows that NH_3 and B_2H_6 start to rise about 500 sec after the sample reaches 90°C . The delay in the release of all these species indicates that a local reaction environment is created in the sample that promotes the decomposition of $\text{NH}_3\text{BH}_3 \rightarrow \text{NH}_2\text{BH}_2 + \text{H}_2$. The formation of this local reaction environment is likely to involve a process that results in the formation of NH_3 and B_2H_6 and takes place on the surface of the sample. Also note the evolution of borazine at a very low rate in this isothermal segment.

In addition to the gas-phase measurements, several hot-stage time-lapse movies were acquired of the decomposition of AB to assess whether geometrical and morphological features play a role in the reaction network. These movies showed that the reaction is not homogeneous throughout the sample and geometrical features play an important role in the decomposition of AB.

By assembling this reaction network we are able to provide insight that can be used to create new ideas on how to optimize and control reaction processes in AB and enable effective and reliable systems.

FIGURE 1. Rates of evolution of selected set of species as AB is heated to and held at 90°C .

Accident Scenarios

We are addressing two contamination scenarios in reactive hydrogen storage systems; breach-in-tank and contaminated refueling. For the past year, we have been considering alane-based systems ($\alpha\text{-AlH}_3$, J. Graetz, Brookhaven National Laboratory). Due to its relatively simple chemistries and limited number of potential reaction pathways, alane provides a unique opportunity to investigate processes experienced during contamination of systems containing reactive high-surface area materials. We have coupled appropriate Knudsen-regime permeability models for flow through packed beds with the fundamental heat transfer and chemical kinetic processes occurring at the particle level (a report describing the oxidation of dehydrogenated-alane was distributed in FY 2009). Using experimental measurement to determine and validate model parameters with tools developed in FY 2008 [3], we have developed a robust numerical model that can be utilized to predict processes in arbitrary scaled-up geometries during scenarios such as breach-in-tank or contaminated refueling.

In FY 2009, we focused on the coupling of our validated mass transfer and chemical kinetic models to systems of scaled-up geometry. Model sensitivity studies were performed for the heat transfer, permeability, and chemical kinetic parameters to determine the confidence levels in process predictions. We have completed our predictions of processes of a dehydrogenated alane tank at high temperature (150°C) for a variety of simulation variables.

To illustrate the use of the coupled model, we chose a model geometry consisting of a cylinder 0.3 m in length and 0.0254 m in diameter with a 2 mm thick stainless steel wall. Simulations were performed with both heat loss to the environment (heat transfer coefficient, $h_w = 5.5, 11 \text{ W/m}^2\text{-K}$) and also adiabatic conditions ($h_w = 0$). Porosity of the bed was varied between 0.5 and 0.76. The impact of radiation from the outer wall ($\epsilon = 0$ to 0.3) and advection in the bed were also considered. The initial temperature and pressure were set to 150°C and $1.01 \cdot 10^{-5} \text{ Pa}$, respectively. The boundary conditions applied to the stem were a pressure of $1.01 \cdot 10^{-5} \text{ Pa}$ for the momentum equation, a temperature of 25°C for the energy equation, and an oxygen concentration of 8.56 mol/m^3 (air) for the species transport equation.

Figure 2 shows six snap-shots in time of the thermal state of the alane cylinder during the contamination process where the cylinder is partially insulated and at an alane porosity of 0.755. A reaction front propagates through the bed with maximum temperatures of approximately 230°C at around 300 seconds. In general, a reaction zone propagates along the entire length of the bed with the exothermicity and extent of the reaction

FIGURE 2. Results for the breach-in-tank scenario simulation for the 80% porous bed indicates a reaction front propagating through the system for 1 hour.

competing with the loss of heat to the environment. The temperature is a maximum within the reaction zone, but overall the temperature decreases with time due to the environmental losses. The maximum temperature in the reaction zone increases with time initially and then decreases for times greater than 300 seconds.

System sensitivities were analyzed by determining the influence of heat loss and packing density on the reaction front characteristics; specifically, the reaction zone temperature and its associated velocity. First, considering the impact of insulation for the 0.76 porous case, perfect insulation results in the highest reaction zone temperature, as might be expected. Interestingly, the reaction zone velocity decreases with increased insulation and temperature due to the kinetics of the reaction and the oxygen transport into the cylinder. As described in the kinetics model, the amount of aluminum that participates in the oxidation process increases with temperature. Meanwhile the transport of oxygen into the cylinder is limited by the small opening in the stem. Thus, as the amount of aluminum available increases it takes more time to consume it, which slows the rate of movement of the reaction zone. That is, the reaction zone velocity is determined by the amount of available aluminum and the transport rate of oxygen into the bed.

To investigate the impact of higher densities on the reaction processes, we considered a partially insulated system at 0.5 porosity as might be more appropriate for engineered systems. The properties for this case were calculated based on the thermal conductivity model and an empirical pore size model. In this case, the lower permeability limits the diffusion of oxygen gas significantly, resulting in lower temperatures compared to the 0.76 porosity case. Interestingly, the impact on reaction zone velocity is reversed compared to the insulation analysis; in this case, lower temperatures result in lower reaction zone velocities. However, the same mechanism that reduced the reaction zone velocity when the insulation was increased is at play when the packing density is increased, i.e. an increase in the amount of available aluminum. In the former case the amount of available aluminum increased due to a larger temperature, while in the latter case the larger packing density itself results in more available aluminum, in spite of the reduction in reaction zone temperature. In addition, the larger packing density reduces the permeability and effective diffusivity of oxygen in the bed, so the transport rate of oxygen is reduced, which also contributes to the slower reaction zone velocity.

Future efforts will consider the behavior of complex metal hydrides to quantify the breach-in-tank reaction processes for alkali-metal containing classes of systems. Additionally, by considering transport within a reversible material (such as sodium alanates [4] or magnesium amide/lithium hydride) we can investigate the impact of a contaminated refueling stream. In this scenario, a hydrogen depleted material is exposed to high-pressure hydrogen with entrained air. While the breach-in-tank contamination processes are dominated by diffusion, the contaminated refueling processes are dominated by convection and thus a larger concentration of reactants is available.

The alane system has provided a unique opportunity to observe the propagation of a reaction front through a hydrogen storage bed during a breach in tank scenario. Because the models were built with through experimental measurement, we are able to consider a variety of scenarios. For example, by coupling in chemical kinetics of hydrogen release, we can investigate the impact of de-hydrogenation of the alane during the breach in tank event. Considering the alane system, the hazard presented by the propagating reaction front is low, resulting in only a moderate exotherm. A complete description of the model and resulting simulation can be found in the proceedings from the 2009 International Conference on Hydrogen Safety by the same authors. Other, more reactive systems may result in a more significant hazard where, if un-mitigated, the breach-in-tank could lead to an over-temperature event causing containment vessel failure or other unfavorable outcomes.

Hazard Mitigation

We are developing low weight, low volume additives in the form of monomers/polymers to mitigate the hazards presented by exothermic bed reaction processes as described above and/or external heat source over-temperature events. We seek to identify low mass-loading additives that can be utilized with reactive solid-state hydrogen storage systems that a) provide a fail-safe during over temperature or contamination scenarios, b) do not detrimentally interact with the storage materials during normal operation, and c) do not inhibit but perhaps enhances, heat and mass transport into and out of the active material and composite structure.

Non-homogeneous mitigation solutions - We have selected potential materials for non-homogeneous solutions consisting of localized material that can be distributed strategically during the over-temperature event. This method could surround the bed to provide encapsulation. This approach involves using unreactive or mildly reactive organics that will melt during an extreme exotherm and flow into and around the storage bed, cutting off access of air to the bed. Two categories of materials are being examined to satisfy this role; crystalline small molecules, and high melting temperature polymers. We have identified a variety of aromatic hydrocarbons as high melting solids and are performing the experiments to determine the application of these materials.

Using sodium alanates as a prototype reactive hydride, a mixture of and anthracene was prepared in 1:1 weight ratios to determine the existence of any interactions between the two chemicals. Since any sodium alanate over-temperature events can occur at temperatures near 200°C, anthracene is an appropriate additive with a melting point of 210°C. The mixture was thermally decomposed thermo-gravimetrically and the results compared to un-modified sodium alanate. Considering pure sodium alanates, hydrogen evolution initiates near 100°C and proceeds with a two step decomposition reaction that completes near 180°C. When the sodium alanate is mixed with anthracene in a 1:1 mixture, the hydrogen evolution is qualitatively similar initially. However, the duration of hydrogen evolution is significantly longer compared to the un-

modified sample. Hydrogen begins to evolve near 80°C (somewhat lower than the unmixed sample). At around 100°C, the first sign of reaction is observed though the formation and subsequent evolution of dihydroanthracene. Sublimation of anthracene is observed near 110°C. Higher molecular weight products begin forming at higher temperatures (~150°C). The hydrogen evolution characteristics from the sample are impacted significantly by the hydrogenation reaction.

Our continued efforts focus in two areas. First, we are investigating the reaction pathways that exist between alanates and the anthracene to guide us in our additive selection process. Secondly, we are performing similar experiments with pyrene and perylene and polymers (polypropylene) to determine the usefulness of these materials as additives. Additionally, we are exploring the option to functionalize these materials through the incorporation of halogenated hydrocarbons that can act as a fire retardant and the use of char forming intumescent materials to form a thick char during combustion.

Homogeneous mitigation solutions - Homogeneous additives that exist as a matrix with the hydrogen storage material are also being developed to act as an over-heat fail-safe. Ultimately, we are seeking to develop a matrix that is functionalized in the following three ways:

- Fire suppression – engineered polymer scaffolds can suppress fire via char formation.
- Scaffolding – immobilization of the bed to inhibit particle sintering, decrepitation, and dust release using low density, high surface area polymer xero-/areo-gels.
- Surface catalysis – modification of hydrogen release/uptake with Lewis-basic monomer used in polymer formulation.

A schematic of the process is shown in Figure 3. Fire suppressants and char forming elements are incorporated into the monomers. An additional monomer with Lewis-basic functionality is included. By varying reaction conditions and monomer ratios, polymerization can yield a micro-porous cross-linked matrix. A number of challenges exist in the development of this tri-functional matrix: a) new monomers with

FIGURE 3. Potential tri-functionalized matrix performs as a hazard mitigation and performance enhancement.

fire-suppressing properties must be synthesized, b) the developed matrix must demonstrate structural rigidity to withstand the life-cycle of the hydrogen storage material, and c) monomers and functional groups must be unreactive during polymerization.

We have developed polymerization conditions for 4-vinyl pyridine and the cross-linking agent divinylbenzene. Low density foams have been made and show enhanced mechanical properties compared to the all-styrene containing foams. We have also synthesized the divinyl aryl ether monomer (DVBPC) as a potential matrix precursor. This monomer was accessed by treating vinyl-benzyl chloride with bis-phenol C in DMF (n, n-di-methyl formamide) in the presence of a base. Attempts to use DVBPC as the cross-linking agent, however, have not been successful. We have also developed conditions for polymerizing vinyl monomers in the presence of various metal hydrides and AB. These composite materials contain approximately 10–20 wt% polymer and appear as hard pucks. Thermal analysis and reactivity experiments are underway to compare hydrogen release properties and “breach-of-tank” scenarios with unsupported hydrides.

Conclusions and Future Directions

This project has demonstrated that, through the use of experiment-based model development of complex reaction and transport processes, hazard scenarios can be investigated for a variety of geometries and system configurations. Based on this understanding, hazard mitigation technologies can be developed to make systems reliable and effective. Towards this end we have discovered that:

- The transport of heat and mass can be well characterized for a variety of hydrogen storage materials including metal hydrides, chemical hydrides, and activated carbons.
- An over-temperature event originating from contamination or external sources could present a hazard during the operation of the hydrogen storage system.
- This impact of this over-temperature hazard may be minimized though the use of mitigating solutions such as reactant-excluding additives.

Based on current Presidential budget request, no additional data will be acquired in FY 2010. A significant amount of data has been accrued investigating the reactivity of complex metal hydrides, treatment of contaminated materials, and mitigating additives. These results will be compiled in a final FY 2010 report.

FY 2009 Publications/Presentations

1. D. Dedrick, M. Kanouff, R. Larson, R. Bradshaw, G. Sartor. “Heat and mass transport in hydride systems - Predictions of processes during operation and accident scenarios” HFC 2009, Vancouver BC, May 31st to June 3rd.
2. D. Dedrick, M. Kanouff, R. Larson, R. Bradshaw, J. Graetz, S. Hwang. “Predictions of solid-state hydrogen storage system contamination processes”, Proceedings from the ICHS 2009, Corsica, Fr. Sept 16–18th, 2009, in press.
3. D. Dedrick, R. Behrens, M. Kanouff, R. Larson, R. Bradshaw, G. Sartor. “The reactivity of hydrogen storage materials in the context of systems” Presentation to the International Energy Agency Task 22, Roma, Italy, October 2008 and Jeju Island So. Korea, April 2009.

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1. D.E. Dedrick, “Chapter 4 - Solid-state hydrogen storage system design” SOLID-STATE HYDROGEN STORAGE: MATERIALS AND CHEMISTRY, Edited by G Walker, The University of Nottingham, UK, Woodhead Publishing Ltd, 2008. ISBN 1 84569 270 5.
2. Behrens, R., Jr., New simultaneous thermogravimetry and modulated molecular beam mass spectrometry apparatus for quantitative thermal decomposition studies. Review of Scientific Instruments 1987, 58, (3), 451-461.
3. D. Dedrick, R. Behrens, M. Kanouff, R. Larson, R. Bradshaw. “IV.E.6 Chemical and Environmental Reactivity Properties of Hydrogen Storage Materials within the Context of Systems” 2008 DOE Hydrogen program annual report.
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IV.E.6 Best Practices for Characterizing Hydrogen Storage Properties of Materials

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Project Start Date: February 7, 2007

Project End Date: Project continuation and
direction determined annually by DOE

(J) Thermal Management

(Q) Reproducibility of Performance

Technical Targets

The goal of this project is to prepare a reference document detailing the recommended best practices and limitations in making critical performance measurements on hydrogen storage materials. This reference document will provide a resource to improve the accuracy and efficiency of critical measurements to aid the projects and ultimately the entire program to achieve or exceed the technical storage targets.

In particular this project is focused on the following target related performance measurements:

- **Kinetics** (Targets: system fill time for 5-kg hydrogen, minimum full-flow rate and start time to full-flow)
- **Capacity** (Targets: gravimetric and volumetric capacity)
- **Thermodynamic Stability** (Targets: maximum/minimum delivery pressure of H₂ from tank and impact on capacity and kinetic related targets)
- **Cycle-life Properties** (Targets: cycle life and cycle life variation)

Objectives

- To prepare a reference document detailing best practices and limitations in measuring hydrogen storage properties of materials.
- The document will be reviewed by experts in the field (International Energy Agency (IEA)/ International Partnership for the Hydrogen Economy, etc.).
- The final document will be made available to researchers at all levels in the DOE Hydrogen Storage Program.

Technical Barriers

This project addresses the following technical barriers from the Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- Technical Targets: On-Board Hydrogen Storage Systems
- Barriers addressed
 - (A) System Weight and Volume
 - (C) Efficiency
 - (D) Durability/Operability
 - (E) Charging/Discharging Rates

Accomplishments

- Established new collaborations with Pacific Northwest National Laboratory, the University of California, Berkeley, and California Institute of Technology.
- Compiled example measurements from the literature to illustrate key issues associated with the four tasks outlined above.
- Performed example measurements on classic hydride materials to illustrate key issues associated with kinetics and other measurements.
- Contributions to this project from world experts have been received including written materials, examples, presentation or editorial review of draft documents.
- Final introduction section 100% complete.
- Final kinetics section 100% complete.
- Capacity section in progress 60% complete.
- Posted final reviewed Preface, Introduction, and Kinetic sections to DOE Web site for world-wide access.
- The current Best Practices document is available on the Web [1].

- Presentation: project H-27 “International standardized testing practices for hydrogen storage materials” IEA Hydrogen Implementing Agreement (HIA) Task 22 Expert Workshop for fundamental and applied hydrogen storage materials development. October, 6–10, 2008, Villa Mondragone, Rome, Italy.

Introduction

The Hydrogen Storage Program goal is the development of hydrogen storage materials that meet or exceed the DOE's targets for the onboard hydrogen storage in a hydrogen-powered vehicle. The growth of research efforts in this field and new approaches to solving storage issues has brought the talents of a wide-range of researchers to bear in solving the grand challenge of hydrogen storage. There is a need to have common metrics and best practices for measuring the practical hydrogen storage properties of new materials that are being developed within the U.S. DOE Hydrogen Storage Program as well as at an international level. H2 Technology Consulting is tasked with creating a clear and comprehensive resource that will provide detailed knowledge and recommendations for best practices in the measurements of these properties.

Approach

This project is a combined approach of documenting the experience the principal investigator and other experts in the field have with these measurements, incorporating examples from the literature, performing experimental measurements to demonstrate important issues, and finally, condensing key information into a concise reference guide. Participation from other experts in the field is being sought out for input, relevant examples, and critical review at all levels.

Results

The first task in this project focused on creating a best practices document for kinetics measurements as well as a general introduction and a preface section of the overall “Best Practices” document. The preface section includes a foreword and terminology used throughout the Best Practices document. The introduction section includes an overview of hydrogen storage materials and the common techniques used to characterize the storage properties of such materials. The kinetics section covers such topics as the overall purpose of kinetics measurements, some basic theory, experimental consideration depending on the purpose of the measurements, methods of measurement, and many details on both material properties and experimental

factors that may strongly influence the final results and conclusions.

In Fiscal Year 2009 these sections of the document were reviewed by many experts and after integration of all comments and edits the final version of these sections was posted on the U.S. DOE Web site. We greatly appreciate the collaborative efforts of Professor Sam Mao and Russell Carrington of the University of California, Berkeley and the work of all of the reviewers: Dr. Gary Sandrock and Dr. George Thomas, consultants to the U.S. Department of Energy; Dr. Michael Miller of Southwest Research Institute® in San Antonio, TX; Dr. Anne Dailly, Dr. Eric Poirier, and Dr. Frederick Pinkerton of General Motors R&D Center; Dr. Ole Martin Løvvik of the Institute for Energy Technology in Kjeller, Norway; Professor Channing Ahn of the California Institute of Technology in Pasadena, CA; and Dr. Nobuhiro Kuriyama and Dr. Tetsu Kiyobayashi of the National Institute of Advanced Industrial Science and Technology in Osaka, Japan. In addition, the work has been coordinated and has received important scientific input through our contract monitor Dr. Phil Parilla at the National Renewable Energy Laboratory.

The next task focused on the capacity section of the “Best Practices” document. For this work collaborations were established with the following contributing authors: Steven Barcelo from the University of California, Berkeley, Justin Purewal from the California Institute of Technology and Abhi Karkamkar from Pacific Northwest National Laboratory. Through this collaboration the document has added perspectives of critical measurement issues from the three main materials research areas: on-board rechargeable chemical hydrides, off-board regenerable chemical hydrides, and hydrogen physisorption materials. The first draft of this section has been completed and sent to several reviewers.

Examples are included below of important considerations when making capacity measurements on different types of materials. Figure 1 shows hydrogen desorption capacity increase for the on-board rechargeable chemical hydride, Ti-doped NaAlH_4 , during initial activation cycles [2]. Several cycles may be required to reach full capacity and materials should not necessarily be overlooked because of poor capacity in only the first absorption/desorption cycle.

Figure 2 shows significant differences in capacity at different temperatures for the off-board regenerable chemical hydride, ammonia borane. Changes in the induction period as a function of temperature are observed and are due to changes in the chemical process pathways at different temperatures [3].

Figure 3 demonstrates the difference between measured excess capacity and the total material hydrogen capacity for metal-organic framework (MOF) physisorption materials [4].

FIGURE 1. Example of activation effects on capacity for hydrogen release from NaAlH_4 doped with pre-reacted Ti additive [2].

FIGURE 2. Dehydrogenation capacity as a function of time and temperature for ammonia borane [3].

Conclusions and Future Directions

In FY 2009 we were able to establish important collaborations and technical assistance from experts in the field. We were able to complete the final version of the preface, introduction and kinetics sections in a timely manner. We are currently working on the capacity section. The first draft of this section has been completed and sent to reviewers. We expect to complete the final version of the capacity section this fiscal year. The following tasks will be the focus of our work in the future:

- Thermodynamics
 - The objective of this task is to establish methodologies for determining equilibrium thermodynamics of hydrogen storage materials.

FIGURE 3. H₂ adsorption isotherms (a) below 1.2 bar and (b) up to 90 bar MOFs 1' (red) and 1m' (blue) at 77 K, and 1m' at 298 K (green). Triangles = Material Excess Capacity. Circles = Total Material Capacity [4].

- We will define measurement protocols to separate true equilibrium conditions from kinetic effects and evaluate new measurement techniques for the rapid determination of thermodynamic stabilities.
- Cycle-life Properties
 - This task will focus on better definitions of how such tests should be performed.
 - We will detail what parameters may impact results, and what properties are the most critical in performance evaluation.

FY 2009 Publications/Presentations

1. Presentation: Gross, K.J., Carrington, R., "Characterization of Advanced Hydrogen Storage Materials: Best Practices in Measurements", International Symposium on Metal-Hydrogen Systems, June 24-28, 2008, Reykjavik, Iceland.

2. Presentation: project H-27 “International standardized testing practices for hydrogen storage materials” IEA HIA Task 22 Expert Workshop for fundamental and applied hydrogen storage materials development. 2–5 March 2008, Sacacomie, Québec, Canada.

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IV.E.7 Standardized Testing Program for Solid-State Hydrogen Storage Technologies

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Contract Number: DEFC3602AL67619

Subcontractor:

Ovonic Hydrogen Systems LLC, Rochester Hills, MI

Start Date: October 1, 2006

Projected End Date: September 30, 2010

Objectives

Overall

- Support DOE's Hydrogen Storage Program by operating an independent, national-level reference laboratory aimed at assessing and validating the performance of novel and emerging solid-state hydrogen storage materials and full-scale systems.
- Conduct measurements using established protocols to derive performance metrics: capacity, kinetics, thermodynamics, and cycle life.
- Support parallel efforts underway within the international community, in Europe and Japan, to assess and validate the performance of related solid-state materials for hydrogen storage.

Current

- Evaluate and validate the sorption capacity and kinetics of Mg-Li-B-N-H storage materials.

- Evaluate the sorption capacity of Pd-doped polyaniline.
- Further assess hydrogen spillover phenomena in metal-doped carbon foam (CF).
- Assess hydrogen spillover in metal-intercalated metal-organic-framework (IRMOF-16).
- Continue round-robin testing in collaboration with the European Union's hydrogen storage program (Novel Efficient Solid Storage of Hydrogen, NESSHY).

Technical Barriers

The technical barriers associated with the operational objectives of the laboratory are:

- Standardization of methods suitable to a wide variety of compositions of matter.
- Development and implementation of "Gold Standard" measurement techniques.

Moreover, this project addresses the following technical barriers from the Storage section (3.3.4.2) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

Verification of material performance

- (P) Lack of Understanding of Hydrogen Physisorption and Chemisorption
- (Q) Reproducibility of Performance

Verification of system performance

- (K) System Life-Cycle Assessment
- (Q) Reproducibility of Performance

(F) Codes and Standards

Technical Targets

This project addresses the fundamental need for establishing a national-level laboratory whose core mission is to study and independently verify the intrinsic sorption characteristics of novel and emerging materials for hydrogen storage, including such activities as they pertain to their use in full-scale storage systems. As a fully qualified laboratory under the purview of the DOE, the laboratory plays a central role in down-selecting materials and systems that emerge from the Centers of Excellence (CoE) and outside entities by:

- Providing in-depth analysis and understanding of hydrogen physisorption and chemisorption mechanistic behavior.
- Determining and validating material and system storage capacities.
- Determining material and system kinetics (charging/discharging rates), thermodynamics, and cycle-life durability.
- Contributing to the testing requirements for codes and standards of full-scale systems.
- Providing listing and labeling services for full-scale systems such as fire safety performance.

Accomplishments

- Evaluated the sorption properties of Pd-doped polyaniline (Pd/PANI) at room temperature, using material provided by the University of Nevada, Las Vegas (UNLV), and determined that the maximum uptake at saturation achievable by this material is only 0.8 wt% at 73 bar with fast kinetics (i.e., equilibrium reached within 30 min).
- Using material prepared by University of South Florida (USF), the multi-component complex metal hydride Mg-Li-B-N-H was extensively evaluated to determine capacity, cycle-life, and chemical stability over four isothermal conditions (373-523 K). Experimental measurements showed:
 - maximum reversible uptake of 5.1 wt% at 75 bar, which was observed at highest temperature (523 K).
 - pressure-composition-isotherms were not consistent with those of classical metal hydrides (i.e., equilibrium plateaus were not observed and uptake was shown to increase with temperature).
 - hydride phase formation was kinetically limited.
 - absorption kinetics exhibited an initial steady-state condition within four hours, followed by slow uptake out to 21 hours.
 - material is chemically stable with no detectable quantities of volatile species during desorption.
- In collaboration with the National Center of Scientific Research (NCSR) “Demokritos” in Greece (NESSHY), room-temperature hydrogen spillover effects in PdHg-doped CFs were further investigated for additional batches of material (CF-3, CF-4). Experimental measurements showed:
 - lower hydrogen uptake above 10 bar than previously measured (CF-1), achieving 2.1 wt% at 88 bar for CF-3.
 - evidence of higher degree of unalloyed Pd in the X-ray diffraction (XRD) pattern than in previous batch.

- significant quantity of water is desorbed from PdHg/CF as determined by laser thermal desorption mass spectrometry (LTDMS), likely due to spillover of atomic hydrogen and subsequent binding to oxygen-bearing carbon atoms in CF.
- broad range of stable binding sites for spilt over hydrogen.
- isotopic (D_2) LTDMS confirmed spillover, binding to oxygen and desorption of water (HDO).
- water desorption also detected under high-pressure volumetric conditions.
- By leveraging SwRI®’s parallel research activities, IRMOF-16 compounds entrapping nanoparticles of Ti, TiB_2 , or $AuAl_2$ (i.e., metal intercalated IRMOF-16) were successfully synthesized. These metal-intercalated MOFs adsorbed as much as 1.3 wt% at 80 bar and room temperature for the Ti-IRMOF-16 compound, possibly attributed to hydrogen spillover, and exhibited relatively fast kinetics (14 min for equilibration).

Introduction

Promising classes of materials being developed for reversible on-board hydrogen storage have emerged, thus compelling a rigorous and independent evaluation of their storage capacity, thermodynamics, and kinetics. Occasionally, entirely new chemistries or structural motifs are discovered that yield unexpected properties which must be further studied or validated. Notably, metal organic frameworks (MOFs) [1], destabilized nitrogen-based metal borohydrides [2], and spillover compounds of MOFs and nanoporous carbon materials [3,4], are examples of materials exhibiting surprisingly favorable storage properties which approach the sought-after material targets for on-board storage (Figure 1).

The laboratory has proceeded to evaluate new materials of importance whose validation of hydrogen storage properties is regarded as a high-priority within the solid-state storage community. The most recent priorities for the laboratory have concentrated on evaluating Pd/PANI, Mg-Li-B-N-H complex metal hydride, and PdHg-doped carbon foams (PdHg/CF). In addition to these DOE directives for validation, internally-sponsored materials development activities have been undertaken to synthesize metal-intercalated IRMOF-16 and evaluate whether chemisorptive strategies for hydrogen storage predicated on spillover can be elicited in such structures. These developments were principally motivated by the need to overcome the diffusion-limited kinetics associated with hydrogen

FIGURE 1. The relative performance of physisorption, spillover, and complex hydride materials towards achieving the minimum material target for on-board reversible fuel storage.

spillover effects in surface catalyzed MOF and carbon materials previously studied [3-5].

Approach

Validating the sorption behavior of storage materials and uncovering the mechanisms involved are approached through close collaboration with researchers among the Materials Centers of Excellence (e.g., the Physisorption CoE), the international community, and SwRI®'s Internal Research & Development Program (IR&D). The laboratory employs a “best practices” approach based on standard operating procedure-documented analytical methods to critically evaluate novel storage materials of potential impact to the sought-after storage goals. By leveraging SwRI®'s IR&D program, fundamental aspects of materials research are addressed where critical knowledge or physical matter is presently lacking. This element of the project provides a venue for the discovery of new materials and the elucidation of unknown mechanisms.

Results

Pd/PANI

The most salient results of our studies over the past year are summarized in Table 1. While only 0.8 wt% uptake was realized at room temperature for Pd/PANI as determined by high-pressure gravimetric analysis, the adsorption and desorption kinetics were both fast, with steady-state conditions typically being achieved under 30 min. Interestingly, an initial conditioning step was required before measureable uptake could be observed. Subsequent sorption cycles demonstrated steep uptake toward saturation at low pressures (<5 bar).

TABLE 1. Overall Summary of Results for Various Classes of Storage Materials Under Investigation

Storage Material	Source	Gravimetric Capacity (wt%)	Comments
Pd/PANI	UNLV	0.8 [298 K, 73 bar]	Fast, reversible kinetics
Mg-Li-B-N-H	USF	5.1 [523 K, 75 bar]	Kinetically-limited phase formation; chemically stable
PdHg/CF	NCSR	2.1 [298 K, 88 bar]	Slow kinetics; evolves water; capacity is sensitive to process variables
Ti-IRMOF-16	SwRI®	1.3 [298 K, 80 bar]	Fast kinetics
TiB ₂ -IRMOF-16	SwRI®	0.2 [317 K, 65 bar]	Thermally activated uptake
AuAl ₂ -IRMOF-16	SwRI®	1.0 [298 K, 65 bar]	Fast kinetics

Mg-Li-B-N-H Complex Hydride

High-pressure volumetric analysis of (Mg-Li-B-N-H), a multi-component composite consisting of three hydrides $\text{MgH}_2/\text{LiBH}_4/\text{LiNH}_2$ (Mg-Li-B-N-H), showed gravimetric capacities and thermodynamic properties that approach the desired targets for reversible storage. In the present case, the highest reversible capacity was 5.1 wt% at 75 bar and 523 K. Compared with literature data for the individual or binary hydride components, the ternary composite capitalizes on lowered desorption temperatures and abatement of the evolution of ammonia from LiNH_2 . Previously reported studies have attributed these properties of the ternary system to a self-catalyzing mechanism in which the products of one reaction nucleate a subsequent reaction [2].

Pressure-composition-isotherms (PCT) for life-cycle experiments carried-out on Mg-Li-B-N-H are shown in Figure 2. In contrast to conventional metal hydrides, plateaus at well defined equilibrium pressures were not readily detected in the PCT curves, which would otherwise be indicative of hydride phase formations. Furthermore, hydrogen absorption is shown in Figure 2 to increase with isothermal temperature. These oddities in the absorption behavior of this ternary composite can be attributed to kinetically-limited phase formation for the conditions under which these measurements were made. Isothermal kinetic profiles measured for absorption and desorption out to 20 h (Figure 3) corroborate the kinetic limitations of phase formation. Desorption at 473 K is relatively fast (<0.05 wt% at 2 h) compared with absorption over the same duration. During absorption, a fast and slow phase is observed, the latter of which shows a steady rise out to 17 h.

FIGURE 2. PCT curves measured for the ternary complex hydride Li-Mg-B-N-H using high-pressure volumetric analysis.

FIGURE 3. Extended Kinetic Profiles Measured at 473 K for Li-Mg-B-N-H

Of particular importance, real-time mass spectrometry measurements performed during PCT life-cycle experiments indicate that volatile species containing boron or nitrogen are not evolved during desorption at 523 K. This result confirms that ternary composites of this kind exhibit chemical stability.

PdHg/CF Spillover Compound

Storage materials predicated on hydrogen spillover effects are under intensive study in our laboratory. In collaboration with NCSR, the storage capacity of PdHg/CF and the spillover mechanism involved was further evaluated in an attempt to validate or reconcile the extraordinary storage capacity (8 wt% at 80 bar and 298 K) reported earlier [6] for the first batch of PdHg/CF (CF-1). Two new batches of CF (CF-3 and CF-4) were synthesized and doped with PdHg nanoparticles for analysis. Prior to volumetric sorption analyses, we attempted to gain additional insights into

FIGURE 4. High-pressure gravimetric and volumetric sorption isotherms measured for various batches of PdHg/CF at room temperature.

the mechanism of hydrogen uptake by conducting inelastic neutron scattering measurements using the TOSCA instrument at the ISIS synchrotron-spallation neutron source (Rutherford-Appleton Laboratory, UK). These experiments proved to be exceedingly difficult to conduct due to the large background scattering signal from dihydrogen versus that of hydrogen bound to the CF.

The results comparing gravimetric and volumetric analyses at room temperature are shown in Figure 4. Significant differences in the uptake capacity between CF-1 and the new material batches (CF-3 and CF-4) were observed (8 vs. 2.1 wt% at 80 bar). Additionally, the capacity in CF-3 diminished with multiple adsorption cycles. This effect was not observed in CF-1, and led us to believe that the catalytic activity of the PdHg nanoparticles was somehow compromised in CF-3 and CF-4. Upon further characterization of this material, powder XRD measurements showed evidence of alloy segregation into pure Pd and Hg on the CF. It is evident that process variables appear to play a significant role in the measured capacity of these CF-based spillover materials, and further work must be undertaken to resolve these variables.

In order to augment our understanding of the sorption properties and binding energies associated with PdHg/CF, LTDMS measurements were conducted with the goals of determining the number of different “high-energy” binding sites, and assessing whether internal conversion of bound hydrogen to yield water occurs as a side reaction of spillover upon desorption. The latter goal was sought on the premise that carbon foams have been shown to contain a high percentage of oxygen. While such oxygenation of the carbon matrix is thought to be conducive to increasing hydrogen (atomic) binding energies, there is the concern that binding of hydrogen to these sites may internally convert to water molecules upon desorption under certain conditions.

FIGURE 5. LTDSMS profile of hydrogen measured for PdHg/CF, indicating multiple, high-energy binding sites.

In Figure 5, we show a typical result of the LTDSMS desorption profile for PdHg/CF following room temperature dosing of hydrogen. The results indicate that high energy binding sites are indeed present in this material and occur between 225 and 250 K. This energy range is further shown to be substantially above physisorbed hydrogen near 175 K. Expansion of the desorption profile (inset) shows multiple peaks which, after spectral fitting, can be deconvolved into five peaks, each one representing a different type of binding site. The smallest difference in energy resolved for these peaks is 0.3 K.

While the LTDSMS measurements strongly support chemisorptive uptake in PdHg/CF via spillover, we also discovered that water is liberated from this material as a consequence of catalytically-mediated internal conversion of oxygen functional groups in the CF receptor. More elaborate LTDSMS studies linked with deuterium dosings showed that neither D_2 nor HD species were desorbed at detectable levels, but that HDO was desorbed at the same temperature as water. These results indicate that D_2 is dissociated by the PdHg catalyst and is spilled over onto the carbon foam receptor. Atomic deuterium then combines with oxygen-bearing carbons (e.g., -OH) and subsequently desorbs as HDO.

Metal-Intercalated IRMOF-16

A better than present strategy for engineering an “ideal” spillover material was envisaged in which metal clusters are intercalated into a three-dimensional nano-architecture. MOFs are particularly attractive in this regard because the pores of the crystalline framework could potentially lead to entrapment of metal particles or clusters within the framework, thereby forming a network of such particles with long-range periodicity

FIGURE 6. High-pressure gravimetric sorption isotherms measured for metal-intercalated IRMOF-16.

and in close proximity to receptor sites for binding of atomic hydrogen. In this pursuit, IRMOF-16 [$Zn_4O(1,4\text{-di}(4\text{-carboxyphenyl})\text{benzene})_3$] compounds entrapping nanoparticles of Ti, TiB_2 , or $AuAl_2$ (i.e., metal intercalated IRMOF-16) were successfully synthesized by in situ entrapment of the metal nanoparticles using an ionic liquid (IL) as a co-solvent. The metal nanoparticles were prepared via direct plasma magnetron sputtering into IL.

In the case of Ti-IRMOF-16 and $AuAl_2$ -IRMOF-16, higher than expected sorption capacities were observed at 298 K (1.2 and 1.3 wt% at 80 bar, respectively). The isotherms shown in Figure 6 are mostly linear, which has been consistent feature of materials exhibiting spillover effects. However, the time required to achieve steady-state conditions at each pressure point was less than 15 min, compared with five hours or more for spillover materials previously investigated [3-5]. Since TiB_2 exhibits a minimum in the density of states at the Fermi level [7], no uptake was observed at 298 K for the intercalated IRMOF-16. At higher temperature (317 K), however, hydrogen uptake, presumably via spillover, could be turned “on” (0.2 wt% at 65 bar), albeit a small amount compared with the Ti- and $AuAl_2$ -IRMOF-16 intercalated compounds.

Conclusions and Future Directions

A renewed interest in complex hydrides can be attributed to the realization that ternary composites of MgH_2 / $LiBH_4$ / $LiNH_2$ exhibit unexpected improvements in thermodynamics, reversibility, and chemical stability. Our measurements indicate that hydride phase formation is significantly limited by kinetics even after this ternary hydride is cyclically conditioned to achieve consistent reversibility. Although this system desorbs hydrogen at lower temperatures than the individual

components, the desorption temperature at which significant quantities of hydrogen can be evolved (523 K) is still too high for practical use. Further improvements in kinetics and thermodynamics are therefore needed.

The potential for chemisorptive strategies via spillover in catalytically-doped nanostructures points to promising opportunities in meeting the DOE on-board storage targets. However, spillover materials have been plagued by exceedingly slow, diffusion-limited uptake and release kinetics. Such diffusion-limited behavior in materials evaluated up to now is principally due to catalyst dispersal being effected by decorating only the surface of a micro- or nanoporous receptor (MOF or carbon). In revisiting metal-doped MOFs as spillover materials, we have shown that entrapping the catalyst in the periodic voids of the framework effectively shortens the diffusion lengths between catalytic centers and a chemisorptive site that lies in close proximity. This arrangement manifests in a dramatic improvement in sorption kinetics that will be explored in other forms of framework compounds.

FY 2009 Publications/Presentations

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3. M.G. Norton, D.N. McIlroy, G. Corti, and M.A. Miller, "Silica Nanosprings – A Novel Nanostructured Material for Hydrogen Storage," *Proceedings of the Clean Technology Conference* **2009**, Houston, TX.
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IV.F.1 A Synergistic Approach to the Development of New Hydrogen Storage Materials, Part I

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award, with the other subprojects being funded through Basic Energy Sciences.

Technical Barriers

This project addresses the following technical barriers from the On-Board Hydrogen Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (B) Weight and Volume
- (C) Efficiency
- (D) Durability
- (E) Refueling Time
- (M) Hydrogen Capacity and Reversibility
- (N) Lack of Understanding of Hydrogen Physisorption and Chemisorption

Technical Targets

The main focus will be on meeting the following specific targets and those in Table 1:

- By 2010, develop and verify on-board hydrogen storage materials achieving storage system targets of 2 kWh/kg (6 wt%), 1.5 kWh/L, fill time of 3 minutes for 5 kg of hydrogen, and \$4/kWh.

Objectives

- Bring together an eclectic group of scientists with experience in materials discovery and theoretical prediction of properties to work on developing new types of hydrogen storage materials.

Particular emphasis is placed on exploring the possibilities of the following types of materials for meeting the 2010 DOE hydrogen storage system targets, especially specific energy, energy density, durability, and uptake and discharge kinetics:

- nanoporous polymers
- nanoporous coordination solids
- destabilized high-density hydrides
- nanostructured boron nitride
- magnesium and light alloy nanocrystals

Note that only the research on nanoporous polymers, nanoporous coordination solids, and destabilized high-density hydrides is funded through this

FY 2009 Accomplishments

- Synthesized and characterized the first beryllium-based metal-organic framework: $\text{Be}_{12}(\text{OH})_{12}(\text{BTB})_4$ with a Brunauer-Emmett-Teller (BET) surface area of 4,020 m^2/g .
- Performed high-pressure H_2 adsorption measurements on $\text{Be}_{12}(\text{OH})_{12}(\text{BTB})_4$, revealing good H_2 storage characteristics at 77 K, with maxima of 6.0 excess wt% at 20 bar and 57 g/L at 50 bar.
- Performed detailed characterization of $\text{Mg}_2(\text{DOBDC})$, a metal-organic framework featuring open Mg^{2+} coordination sites H_2 within air-free $\text{Zn}_4\text{O}(\text{BDC})_3$, revealing an initial isosteric heat of H_2 adsorption of ca. -12 kJ/mol and binding of D_2 at a distance of 2.5 Å from the metal center.
- Synthesized and characterized a series of metal-organic frameworks of the type $\text{M}_3(\text{BTC})_2$ ($\text{M} = \text{Cr}, \text{Mn}, \text{Co}, \text{Zn}, \text{Mo}$) featuring open metal coordination sites.

TABLE 1. On-Board Hydrogen Storage System Targets (**Data is based on material only, not system value)

Storage Parameter	Units	2010 System Target	Fiscal Year 2009 materials**
Specific Energy	kWh/kg (wt% H ₂)	2.0 (6 wt%)	7.1 excess wt% at 77 K and 40 bar for air-free Zn ₄ O(BDC) ₃ (SA 3,800 m ² /g)
Specific Energy	kWh/kg (wt% H ₂)	2.0 (6 wt%)	11.5 total wt% at 77 K and 170 bar for air-free Zn ₄ O(BDC) ₃ (SA 3,800 m ² /g)
Specific Energy	kWh/kg (wt% H ₂)	2.0 (6 wt%)	2.3 wt% at 298 K and 70 bar for air-free Zn ₄ O(BDC) ₃ (SA 3,800 m ² /g)
Energy Density	kWh/L (g H ₂ /L)	1.5 (45)	77 g H ₂ /L at 77 K and 170 bar for air-free Zn ₄ O(BDC) ₃ (SA 3,800 m ² /g)
Specific Energy	kWh/kg (wt% H ₂)	2.0 (6 wt%)	6.0 excess wt% at 77 K and 20 bar for Be ₁₂ (OH) ₁₂ (BTB) ₄ (SA 4,020 m ² /g)
Energy Density	kWh/L (g H ₂ /L)	1.5 (45)	57 g H ₂ /L at 77 K and 50 bar for Be ₁₂ (OH) ₁₂ (BTB) ₄ (SA 4,020 m ² /g)
Specific Energy	kWh/kg (wt% H ₂)	2.0 (6 wt%)	3.8 wt% at 77 K and 45 bar for hypercrosslinked polystyrene (SA 1,930 m ² /g)
Specific Energy	kWh/kg (wt% H ₂)	2.0 (6 wt%)	1.9 wt% at 77 K and 23 bar for hypercrosslinked polyaniline (SA 630 m ² /g)

SA - surface area

- Generated N-linked microporous polymers exhibiting extremely small pore sizes, leading to an initial isosteric heat of adsorption of ca. -18 kJ/mol.
- Investigated new methods for synthesizing hypercrosslinked polypyrroles. With a BET surface area of 732 m²/g, the best sample exhibited reversible H₂ uptake of 1.6 wt% at 77 K and 40 bar.
- Utilized computational methods in examining changes in H₂ binding energies within the clusters [M₄Cl(tetrazolate)₈]¹⁻ (M = Mn, Cu, Zn).
- Investigated hydrogen storage in mixtures of MgH₂ and MgF₂. With 3 mol% MgF₂, the results showed desorption performance very similar to the results previously obtained with 10 mol% MgF₂.
- Performed elemental mapping by electron energy loss spectroscopy (EELS) to show that in the 3 mol% samples, the fluoride is well dispersed over the particle surface.

Introduction

Known hydrogen storage materials exhibiting promise include nanostructured carbon-based solids,

chemical hydrides, and metal hydrides. Although worthy of significant further investigation, it is by no means clear that any of these systems will be able to meet the DOE performance targets for 2010. We are therefore undertaking a broad-based and coordinated effort to search for new classes of hydrogen storage materials.

Approach

The combined team of UCB and LBNL have formed a collaborative, interdisciplinary group to research promising nanostructured materials for hydrogen storage. A total of eight themes or subprojects are currently underway; the following four are funded through this award:

- Synthesis and characterization of nanoporous coordination solids (Long).
- Synthesis and characterization of nanoporous polymers (Fréchet).
- First-principles determination of H₂ binding energies with predictive applications in design of new nanoporous hydrogen storage materials (Head-Gordon).
- Synthesis and characterization of destabilized high-density hydrides (Richardson).

Our approach will be to explore numerous possibilities for new materials, and narrow our focus as the research progresses. The synergy of many scientists in one location working toward a common goal is expected to accelerate our progress and lead to new ideas via cross-fertilization.

Results

Microporous Metal-Organic Frameworks – Until recently, our reports have mainly focused on the synthesis of metal-organic frameworks comprising transition metal atoms or clusters as building blocks. We have recently initiated a survey of group 2 and 13 main group elements, namely beryllium, magnesium, calcium and aluminum, as potential candidates for building light-weight materials. The interest in these compounds is strongly coupled with the expectation that their high charge-to-size ratio will provide more polarizing metal centers to serve as high-enthalpy adsorption sites for hydrogen molecules.

Beryllium perhaps represents the ultimate lightweight main group element for building metal-organic frameworks, and we are currently unaware of any examples of extended porous structures incorporating this element. In our previous report we described in detail the synthesis, characterization and preliminary hydrogen storage properties of a novel beryllium-based metal-organic framework,

$\text{Be}_{12}(\text{OH})_{12}(\text{BTB})_4$ (**1**, BTB^{3-} = 1,3,5-benzenetribenzoate), shown in Figure 1.

The physical properties of activated single-crystalline samples of **1** have been recently studied. The BET surface area is 4,020 m^2/g (Langmuir 4,400 m^2/g), which is the highest recorded so far for a main group metal-organic framework. This far exceeds the value of approximately 1,000 m^2/g we reported for the same compound in our previous report, highlighting the importance of optimizing the synthetic and activation procedures. The current result broadly agrees with the accessible surface area computed from the crystal structure of approximately 3,600 m^2/g . Samples of **1** allowed to stand in air following activation showed no decomposition over 12 h, which is a contrast to other high-surface area materials such as $\text{Zn}_4\text{O}(1,4$ -

benzenedicarboxylate) (MOF-5) which degrades rapidly upon exposure to the air.

The hydrogen storage properties of **1** have also been examined. As shown in Figure 2, the uptake recorded at 1 bar of hydrogen at 77 K is 1.6 wt% (1.3 wt% for MOF-5 under the same conditions), and the profiles are indicative of a low isosteric heat of adsorption. Indeed, a virial fitting of the experimental data yields an initial isosteric heat of adsorption of approximately 5.5 kJ/mol. While this result precludes hydrogen storage at room temperature, which requires an isosteric heat of adsorption of approximately 20 kJ/mol, it is promising for cryogenic storage applications. High-pressure hydrogen uptake measurements at 77 K have indicated that this is the case, with approximately 6.0 excess wt% adsorbed at 20 bar, and 8.0 total wt% adsorbed at 40 bar (see Figure 2). The volumetric storage capacity of 57 g/L is competitive with the most effective metal-organic frameworks in cryogenically storing hydrogen.

We have also begun a hydrogen uptake study on the recently reported magnesium-containing framework, $\text{Mg}_2(\text{DOBDC})$ (H_4DOBDC = 2,5-dihydroxyterephthalic acid). This compound is of interest due to the presence of unsaturated coordination sites on the Mg^{2+} ions, which may act as strong binding sites for hydrogen. Initial experiments have indicated that the initial isosteric heat of adsorption for hydrogen in this compound is 11–12 kJ/mol, and the hydrogen uptake in the low-pressure region is high (>2.5 wt% at 1 bar). Although this compound and a number of its isostructures has been the subject of a hydrogen adsorption study, both the binding strength and hydrogen uptake is higher in our hands, possibly highlighting the importance of using the correct synthetic and handling procedures when performing manipulations on this compound. We are currently performing further studies on the hydrogen binding sites

FIGURE 1. A portion of the single-crystal structure of $\text{Be}_{12}(\text{OH})_{12}(1,3,5\text{-benzenetribenzoate})_4$, **1**, projected along the crystallographic *c*-axis (left) and *b*-axis (right). Blue, gray, and red spheres represent Be, C, and O atoms, respectively. H atoms have been omitted for clarity.

FIGURE 2. High-pressure hydrogen uptake data for $\text{Be}_{12}(\text{OH})_{12}(1,3,5\text{-benzenetribenzoate})_4$, **1**.

in this compound by infrared and Raman spectroscopy, and neutron diffraction in collaboration with the National Institute of Standards and Technology (NIST). While these experiments are ongoing, initial results from the neutron diffraction experiments have allowed us to locate the hydrogen atoms within the structure, with the centroid of the H_2 molecule located approximately 2.5 Å from the Mg^{2+} site. It is hoped that the results of these studies will allow us to better understand the nature and strength of the interaction between hydrogen and the unsaturated metal site, and furthermore, the knowledge gained may serve as a basis for designing new target materials for use as hydrogen storage materials.

The adsorption enthalpy for hydrogen binding to activated metal-organic frameworks is one of the limiting factors for accessing appreciable storage of this gas at ambient temperature. To ascertain which metal ion affords the maximal hydrogen binding enthalpy, we have continued to focus on synthesizing and characterizing the gas-uptake properties of a series of isostructural frameworks in which only the metal is varied. Frameworks containing dimetallic clusters bridged by four carboxylate groups are attractive targets as this building unit is a common motif in coordination chemistry.

The synthesis of $Zn_3(BTC)_2$, $Cu_3(BTC)_2$, $Cr_3(BTC)_2$ and $Mo_3(BTC)_2$ were reported previously, either in the literature or communicated by our lab. The chromium(II) framework shows a moderate hydrogen binding enthalpy at -6.8 kJ/mol with a gravimetric storage capacity of 2.1 wt% at 77 K. Powder neutron diffraction experiments carried out at NIST on activated $Cr_3(BTC)_2$ indicate that hydrogen binds tightly to a hydrophobic pocket within the framework as well as the exposed metal center. Rietveld analysis revealed a short distance between the metal ions (2.05 Å) that lengthens upon hydrogen binding (2.17 Å). Together with a moderate adsorption enthalpy (-6.8 kJ/mol), these data suggest that there is bonding between the chromium(II) ions which, expectedly, weakens hydrogen binding at the vacant axial coordination site. Hydrogen uptake by $Zn_3(BTC)_2$ might be predicted to be greater than the chromium(II) analogue because no metal-metal bond exists in the former. However, attempts to activate the zinc(II) framework by evacuating guest solvent at elevated temperatures resulted in a loss in crystallinity and porosity. We are currently exploring alternate methods for activating this material, such as treatment with supercritical carbon dioxide.

Recently, we have synthesized $Mn_3(BTC)_2$ and $Co_3(BTC)_2$, which was confirmed by powder and single-crystal X-ray diffraction experiments that these compounds are isostructural with other $M_3(BTC)_2$ frameworks. Infrared spectra of the solid strongly suggest that the open-coordination site at the metal ion is occupied by *N,N*-dimethylformamide (DMF).

Typically, these DMF molecules are exchanged for lower boiling alcohol solvents, which allows for milder desolvation temperatures. These frameworks however lose crystallinity as observed by changes in the powder X-ray diffraction patterns upon exposure to air or soaking in protic solvents. At present, we are investigating conditions to increase the current synthetic scale and activate these compounds for hydrogen-uptake measurements.

Microporous Polymers – We continued our studies focused on the preparation of hypercrosslinked polymers with large surface areas. The concept of the hypercrosslinking requires that the polymer to be crosslinked must be dissolved or swollen with a solvent and then crosslinked at a reaction rate that is faster than the rate of desolvation of the polymer chains. If this condition is not met, the resulting polymer is not porous.

In our specific study, we targeted networks consisting of aromatic rings held in a porous framework by the smallest possible linking groups. The reasons for this approach were twofold. First, we have shown previously that nanoporous polymers prepared via hypercrosslinking using smaller, more rigid crosslinks exhibit higher surface areas than those synthesized with longer less rigid crosslinks. Second, smaller crosslinks add less non-adsorbing mass to the final porous material. We also wanted to avoid the presence of electron withdrawing substituents on the aromatic rings since we have already demonstrated that addition of electron withdrawing groups to aromatic rings decreases their ability to physisorb hydrogen.

The simplest approach to forming networks consisting of aromatic rings starts with precursors containing reactive groups directly attached to the aromatic ring such as aryl halides and amines, which can be coupled using a variety of synthetic routes. For example, the Ullman reaction catalyzed with soluble or insoluble copper salts and the Buchwald reaction which relies on soluble palladium catalysts are used often to perform such couplings. Both of these syntheses were applied to the crosslinking of aryl amines with polyhalogenobenzenes to form amine-linked networks of aromatic rings. Thus crosslinking with tribromobenzene affords networks of di- and tri-functionalized aromatic rings connected by amines whereas crosslinking with diiodobenzene or dibromobenzene leads to a network of difunctionalized aromatic rings. While the substituted benzenes can be considered crosslinkers from the synthetic point of view, the final product is in fact a network of aromatic rings connected through nitrogen atoms. The resulting porous polymer networks consist of aromatic rings linked through a trivalent nitrogen atom. The Buchwald reaction appears to be more effective than the Ullman synthesis for the production of such materials. The use of solvents with higher Hildebrand solubility coefficients during synthesis affords polymers

with higher surface areas. The nanoporous polymers possess unusually high initial enthalpies of adsorption of hydrogen reaching values of up to -18 kJ/mol which appear suitable for the adsorption at temperatures higher than 77 K. Hypercrosslinked polymer networks we synthesized contained 37-92% of pores small enough for hydrogen adsorption but too small to allow penetration of nitrogen thus enabling size-selective gas adsorption.

We have also synthesized a series of nanoporous polypyrroles using a variety of different crosslinking units to control pore size. For example, polypyrrole base was crosslinked with diiodomethane. With remarkably high BET and Langmuir surface areas of 732 and 543 m²/g, the resulting polymer reversibly adsorbs 1.6 wt% hydrogen at 77 K and 0.4 MPa. In order to explore the effect of the number of bonds linking the crosslinker with polypyrrole on the porous properties of our materials, we also used iodoform to crosslink polypyrrole base. This reaction produced materials which reversibly adsorb 1.3 wt% H₂ at 77 K and 0.4 MPa and exhibits BET and Langmuir surface areas of 401 and 436 m²/g, respectively. The amount of residual iodine in the final product is undetectable by elemental analysis.

Polypyrrole was also hypercrosslinked with boron. This novel synthesis results in a mixture of polypyrrole rings crosslinked with boron atoms. Although crosslinking was incomplete, this polymer exhibits BET and Langmuir surface areas of 19 and 233 m²/g. Although the largest reported, the surface area of our polymers was relatively small and the polymer adsorbs only 0.6 wt% hydrogen at 77 K and 0.1 MPa. Therefore, we continued the study in order to optimize the choice of both solvent and base. Unfortunately, good solvents of polypyrrole such as dimethylformamide, N-methyl pyrrolidinone, and dimethyl sulfoxide could not be used as they react violently with boron triiodide, while solvents that are typically used with borohalides like diethyl ether and tetrahydrofuran, are very poor solvents for polypyrrole. Finally, toluene, which is a mediocre solvent for polypyrrole but only forms weak complexes with boron triiodide was selected. The choice of bases also requires some compromises as hindered organic bases such as triethylamine and diisopropylethylamine react rapidly with boron triiodide while most inorganic bases have little solubility in toluene. Thus, a very fine powder of cesium carbonate was chosen as the optimal base for this reaction.

However, we prepared again polymer with nanoporosity enabling exclusion of gas molecules larger than hydrogen based on their size. For example, the adsorption of hydrogen was about 5 times higher than that found for nitrogen. This result is important since it may enable selective adsorption of pure hydrogen from its mixtures with other gases that are typically present in the industrially produced hydrogen.

We also tested additional metals to achieve hypercrosslinking and form a metal-organic network. For example, iron trichloride crosslinks polypyrrole in the presence of dimethylsulfoxide and sodium t-butoxide. This reaction so far affords a polymer with a relatively low BET surface area of 116 m²/g.

Computational Studies of H₂ Binding – We have been engaged in modeling the hydrogen-binding center in the compounds synthesized in the Long group, beginning with Mn₃[(Mn₄Cl)₃(BTT)₈(CH₃OH)₁₀]₂ (H₃BTT = 1,3,5-tris(tetrazol-5-yl)benzene). From there, we moved to consider both substitutional replacements of the Mn²⁺ counterion, as performed experimentally, and substitutional replacements of the central (Mn₄Cl) unit with (Zn₄Cl) and (Cu₄Cl) units. A single site, with tetrazolate anions replacing the BTT ligands is treated. In the experimental compounds, these binding centers are overall negatively charged, which is compensated by dications that populate half the sites. We have worked through and substantially resolved most of the computational protocol issues associated with appropriate selection of density functional, integration grid, and treatment of the metal center. A large series of calculations is underway treating sites of both charges and the various substitutional replacements. We anticipate being able to complete both detailed comparison against existing experimental data, as well as provide some indication of the scope for improved binding coming from alternative metals.

Destabilized Metal Hydrides – We reported previously that addition of 10 mol% magnesium fluoride to magnesium hydride enhanced the sorption/desorption kinetics and greatly improved the utilization of MgH₂. This has now been extended to mixtures containing 3 mol% and 1 mol% MgF₂. The desorption behavior at 673 K for the three mixtures and for commercial MgH₂ are shown in Figure 3. The results are near theoretical

FIGURE 3. Effects of addition of MgF₂ on MgH₂ hydrogen desorption.

for 10% and 3% MgF_2 , the higher percentage for the latter due to the increased weight percentage of active MgH_2 . The improved performance persisted at a more constant level for the 3% case. While 1% addition had a positive effect on the utilization, the added weight reduced its capacity relative to pure MgH_2 , and the kinetics were worse. We believe that this is due to incomplete dispersion of the MgF_2 on the MgH_2 surfaces.

Elemental mapping by electron energy loss spectroscopy (EELS) of a ball-milled 3% MgF_2 sample showed that the fluoride was well dispersed over the particle surface (see Figure 4). As no evidence has been found by X-ray diffraction for dissolution of fluoride in the hydride or metal phases, we postulate that the mechanism by which fluoride acts is to coat the surfaces and prevent coarsening and sintering of Mg during desorption. This then enhances hydrogen uptake by maintaining the metal as small particles. High-resolution transmission electron microscope images of hydrogen-desorbed fluoride-treated Mg particles showed sharp faceting with a small grain size. On the other hand, without fluoride, sintering and coarsening reduced the surface area and contribute to isolation and poor utilization of Mg.

Fluoride addition appears to be a simple and inexpensive route to improving the hydrogen storage properties of magnesium hydride. Unlike metal catalysts, its effects persist over many cycles due to its mode of action on the particle morphology rather than on hydrogen splitting and recombination.

Conclusions and Future Directions

Synthetic approaches have now been developed for incorporating high concentrations of metal carbonyl units within nanoporous coordination solids and polymers. Methods for displacing CO are now under investigation, and will be followed by H_2 storage measurements for these unique materials. In addition, electronic structure calculations are underway to assess the best combinations of metal center and ligand substituents to adjust the H_2 binding energy.

FY 2009 Publications

1. "Hydrogen Storage in Microporous Metal-Organic Frameworks with Exposed Metal Sites" Dinca, M.; Long, J.R. *Angew. Chem., Int Ed.* 2008, 47, 6766-6779.
2. "Preparation of Size-Selective Nanoporous Polymer Networks of Aromatic Rings: Potential Adsorbents for Hydrogen Storage" Germain, J.; Fréchet, J.M.J.; Svec, F. *Chem. Mater.* 2008, 20, 7069-7076.
3. "Nanoporous, Hypercrosslinked Polypyrroles: Effect of Crosslinking Moiety on Pore Size and Selective Gas Adsorption" Germain, J.; Fréchet, J.M.J.; Svec, F. *Chem. Commun.* 2009, 1526-1528.

FIGURE 4. EELS maps showing the uniform, but granular distribution of MgF_2 particles on the surfaces of dehydrided Mg grains.

4. "Hydrogen Storage in Metal-Organic Frameworks" Murray, L.J.; Dinca, M.; Long, J.R. *Chem. Soc. Rev.* 2009, 38, 1294-1314.
5. "Nanoporous Polymers for Hydrogen Storage" Germain, J.; Fréchet, J.M.J.; Svec, F. *Small* 2009, 1098-1111.

FY 2009 Presentations

1-16. “Hydrogen Storage in Metal-Organic Frameworks”
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IV.F.2 Capacitive Hydrogen Storage Systems: Molecular Design of Structured Dielectrics

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Project End Date: September 30, 2011

Objectives

To develop storage materials that enable high H_2 loading under more economical temperature and pressure ranges; that have controllable uptake/release dynamics; and that have moderate thermal management requirements. By using electric field enhanced adsorption, we hope to:

- Address thermal management issues (10-15 kJ/mole electric-field effect expected).
- Ultimately meet hydrogen loading goals at more practical combinations of temperature and pressure.
- Establish better control over charge/discharge dynamics via field modulation.

Technical Barriers

This project addresses the following technical barriers from the Storage section (part 3.3) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (C) Efficiency
- (E) Charging/Discharging Rates
- (J) Thermal Management
- (P) Lack of Understanding of Hydrogen Physisorption and Chemisorption

Technical Targets

This project is conducting fundamental studies on hydrogen adsorption in porous adsorbents under the influence of externally applied electric fields. Electric field enhancement provides a new route towards the meeting the 2015 system capacity targets of 5.5 percent hydrogen by weight and 40 grams hydrogen per liter and the ultimate system targets of 7.5 percent hydrogen by weight and 70 grams hydrogen per liter. Electric-field enhancement of binding (i.e. capacitive storage) integrates well with electric drive systems and the insights gained from these studies will be applied toward the design and synthesis of storage materials that will be more likely meet the DOE hydrogen storage targets. Outcomes of this work are expected to include:

- New insights into H_2 physisorption/chemisorption at sites of high local polarizability.
- Improvements in net efficiency of storage systems, i.e. acceptable hydrogen wt% at more accessible temperature and pressure.
- Better control over hydrogen charge/discharge dynamics (field strength is now a control variable in addition to thermal and pressure modulation).

Accomplishments

During year 1, the project team has:

- Initiated a series of ab initio computations to explore the effects of external fields on electron density in organic constituents typical of metal organic frameworks (MOFs). Baseline electronic structure calculations have also been performed on Cu-BTC MOF, with an external electric field to be imposed in the subsequent round of calculations.
- Fabricated and tested several capacitor designs for use in measuring sorption under action of an electric field. Sorption measurements are underway.
- Developed technique for densifying adsorbent material that avoids structural damage.
- Began characterizing dielectric properties of porous adsorbent materials using electrochemical impedance spectroscopy. Static dielectric constant, loss tangent, and the breakdown potential are all being measured.
- Completed initial design of a neutron diffraction cell for simultaneous static electric field application. Will ultimately provide insight into specific binding site locations.

Measured isosteric heats of sorption in MOFs are typically on the order of 10 kJ/mol or less. Our calculated value for hydrogen binding at the copper site in Cu-BTC is 8 kJ/mol. Simple thermodynamic calculations suggest that heats of the order of 15-25 kJ/mol will be required for an efficient hydrogen storage material. Thus 100-300% enhancement of binding over zero field must ultimately be achieved. This enhancement in binding can occur at either, or both, metal sites of polarizable organic sites (e.g. the organic linkers found within the MOFs).

Introduction

The concept of capacitive storage involves establishing an electric field across a porous dielectric material specifically designed to adsorb hydrogen. The field then acts on localized regions of high polarizability to enhance hydrogen binding within the cavities of the porous network through induction and dispersion forces. Upon discharge of the “capacitor,” the electric field is removed, and in turn, the induced electrostatic moment required to stabilize hydrogen dissipates. Thus the thermodynamic driving force for binding can in principle be switched on and off at will. As a consequence, the uptake/release dynamics are no longer solely dependent on thermal diffusion processes as much of the energy required to bind and release hydrogen is reversibly introduced into the system in the form of an electric field. Two critical operational issues associated with hydrogen storage are potentially addressed with capacitive storage – hydrogen density and thermal management. Electric field-mediated storage has the ability to enhance the density of stored hydrogen at accessible temperatures and pressures. By applying and releasing the molecular binding energy in the form of voltage (i.e. via the field), the requirements for thermal management of hydrogen uptake and release are lessened. Operating over the range -40 to 60°C should become less onerous since the system is no longer critically dependent on externally supplied thermal flux. Charging and discharging, system cycling, and transient system response now involve field modulation as opposed to just direct heat exchange through the entire bed. The other outstanding issues detailed in the On-Board Hydrogen Storage System Technical Targets, such as delivery pressure, charging/discharging kinetics, and system fill time may also benefit.

The interaction between hydrogen and a porous dielectric host under action of an electric field arises from a number of terms. First, one can consider “static” terms, that are not a function of the field. These represent a baseline and include van der Waals interactions and permanent charge-quadrupole terms. Alone these appear to be insufficient to produce a good hydrogen storage material. Then there are terms that

are a function of electric field, but not of the dielectric substrate. These include the interaction between the field and the permanent H₂ quadrupole. Finally, are the terms that are a function of field and the substrate. These are interactions that we can hopefully tune via structural modification. The simplest of the many possible terms here is the induced dipole-induced dipole term (e.g. an field-induced dipole within a MOF structural element and an induced dipole in the hydrogen). The magnitude of the induced dipoles is proportional to local field and the polarizability tensor. The interaction between the two dipoles, which falls off as r^{-3} , can then be calculated. By tuning the polarizable structural elements to have the highest polarizability in the direction of interaction with hydrogen, we can increase this term. Our manipulation strategy is based on the proportional relationship between polarizability and the volume of electron density (which depends in turn on the radius of the local structural moiety). The polarizability can then be related to the proximity of excited state and local chemical bonding (e.g. lowest unoccupied molecular orbital - highest occupied molecular orbital or band gaps). The molecular-level properties can then be mapped to bulk dielectric response using classical electrostatics (e.g. the Debye equation).

Approach

It is known that manipulation of temperature and pressure provides benefits in hydrogen storage, however, it appears that combinations of these two intensive variables alone will not likely yield the desired end result, namely, high loading under moderate (and economically attractive) conditions. As an alternative, we are examining the effects of also introducing an electric field to enhance hydrogen uptake in porous dielectric substrates. This materials discovery effort is based on the idea that local regions of high electron polarizability will respond strongly to an applied external field. In doing so, the expectation is that the resulting redistribution of electron density will enhance hydrogen binding. This may involve a combination of lower binding energies, creation of new binding sites and/or formation of hydrogen clusters (as is reported in clathrate-hydrate cages [1]). The key challenge then is to localize polarizability within porous adsorbents in order to produce a high dielectric response adjacent to, or within, sub-structures (e.g. cavities) favorable to gas uptake through adsorption or molecular clustering.

Electrostatic stabilizing forces can be locally enhanced by judiciously increasing the polarization of the host substrate at specific sites. The MOFs will serve as one starting point for developing the new dielectric materials [2]. MOFs are composed of metal ions with coordinated organic ligands, where the nature of metal-to-organic ligand coordination provides

versatility in the design and control of chemical and physical characteristics (e.g. local polarizability). Thus in addition to being high surface area structures (up to 3,000 m²/g) MOFs can be chemically tailored by changing the organic links between metal centers. This can be done through introduction of more polarizable atoms and functional groups, tuning the band gap, and/or varying core metal electronic properties. Other related materials such as the zeolitic imidazolate frameworks (ZIFs) will also be considered as candidate adsorbents. Other candidate adsorbents include composites constructed by distributing small metal or semi-conducting clusters in porous structures (e.g. xero- or aero-gels) as another means of producing inorganic materials with extreme dielectric properties [3]. These metal-loaded gels consist of open pore structures that can be impregnated with small metal or semi-conducting clusters to just below the percolation threshold (at the percolation threshold, an electrical short would then develop). The resulting cluster-loaded gels should be insulator-conductor composites capable of large space charge polarization and thus high dielectric response, since they possess ample free electrons within the clusters to readily react to an imposed electric field. Our approach to developing these materials (structured dielectrics) combines both computational guidance and experimental probes.

Results

Static polarization calculations were the first of the computational exercises used as guidance. Several simple substituted benzene molecules (often found in MOF organic linkages) were examined to assess which functionalities are the most promising with regards their charge polarization properties under an applied electric field. These calculations were performed using the Gaussian03 software. Preliminary results suggested that there was little dependence of the calculated dipole polarizability on whether electron withdrawing or electron donating substituents are present. Rather, trends indicated that the stronger effect is that of how many substituents are present (i.e. the total number of electrons in the system) and hence the volume of electron density that is available to respond (be polarized) under action of the field. Reductions in the hydrogen binding energy were indicated, provided the electron density and field strength were both high.

Building on this initial work with simple molecular models of substituted benzenes interacting with a hydrogen molecule in an electric field, we expanded the computational study to now consider molecular fragments of MOF structures. Previously, we have performed calculations on the binding site geometry and thermodynamics of hydrogen in the Cu-BTC MOF structure. The crystal structure of Cu(II) acetate provides a useful starting point for the construction

of a molecular model containing a structural unit from the Cu-BTC structure (Figure 1a). Cu-BTC has several predicted binding sites for the hydrogen molecule in the absence of an electric field, including at the open-coordination Cu(II) site and in the vicinity of the organic spacer. Our initial calculations place the hydrogen molecule at the metal site in a side-on geometry as shown in Figure 1b. Calculations are now being performed using the MP2 perturbation method (MP2/6-31G for ligands and LANL2DZ for the Cu) within the Gaussian03 software, since our initial calculations showed the importance of including electron correlation in the calculation to account for weak dispersion interactions. We are also considering both the singlet and triplet spin states for the Cu(II)-Cu(II) unit. Full geometry optimization of all the models is being performed with basis set superposition error to calculate the binding sites and binding energies. Once these calculations are completed, an electric field will be applied along the Cu-Cu vector to assess the enhancement of the binding energy.

Dielectric material synthesis efforts were initiated. A laboratory was configured for the preparation of analytical test samples (initially these will include inorganic zeolites, MOFs, ZIFs, and porous carbonaceous materials) for baseline testing activities.

FIGURE 1. Models used in initial Cu-BTC calculations. (a) Simplified molecular model for structural building unit in Cu-BTC. (b) Calculated binding site for H₂ at Cu(II) center.

The laboratory enables us to synthesize of new ligands with the aim of altering framework polarizability. To date, 12 different materials from four material classifications have been prepared and are ready for electrochemical and storage testing. A small metal-insulator-metal capacitor bank was also constructed as the first-generation capacitor test rig. A series of thin copper sheets were used as the capacitor plates, as shown in Figure 2. Once loaded (e.g. with a MOF), the capacitor bank can be inserted into a pressure vessel that provides a small headspace and fitted with temperature probes, high accuracy pressure gauges. The stainless steel pressure containment vessel is also equipped with high voltage electrical leads. Several other test capacitors were also designed and fabricated (see Figure 2).

Early experiments involving the metal-insulator-metal capacitor made use of as-synthesized MOF powders. Packing and granular flow problems during loading of the capacitors led to a lack of reproducibility in tests using powders. Thus, formation of higher density, and reproducibility, was pursued. However, a natural question was the following. Are these candidate materials, which involve rather wispy frameworks, mechanically robust enough to withstand pelletizing as part of a testing protocol? Initial tests suggest that MOF structures do maintain their crystalline nature following pressing into pellets, as shown in Figure 3. Dielectric materials testing is now performed using pressed materials that provide higher density and avoid the granular packing issues.

Gas adsorption experiments are underway using these capacitor test rigs. The effect due to the electrostatic moment in the gas is also being explored by examining adsorption of nitrogen and carbon dioxide, which have significantly different electrostatic moments than hydrogen (e.g. the relative quadrupole moments are: CO_2 - 4.3 electrostatic unit of charge, esu; H_2 - 0.662 esu [4]). Based on the initial screening results, the chemical composition, packing density and physical properties (pore size/volume) of the adsorbent appear to be important, as expected, along with the dielectric response of both the substrate and gaseous species. One potentially important issue we hope to resolve is the relative importance of the crystallographic orientation of the solid adsorbent. One would expect that if the adsorbent has an ample supply of mobile electrons capable of responding to the imposed field, that crystallographic orientation would not govern the net response. Additional work is needed to establish this. Also, by year's end, we expect to have an initial quantitative assessment of the electric field enhancement on hydrogen adsorption in selected MOFs.

In order to characterize the dielectric properties of the adsorbents and ultimately correlate with adsorptive capacity under an applied voltage, dielectric properties are being measured over a wide frequency bandwidth

FIGURE 2. Capacitor cells for testing electric field enhanced adsorption. A metal-insulator-metal capacitor (left); glass cell with internal parallel plate capacitor designed to fit Brunauer-Emmett-Teller apparatus (middle); a custom designed spring-loaded cell to hold pressed pellets during adsorption and dielectric measurements (right).

FIGURE 3. A pressed (densified) copper-based MOF (blue pellet; 1/4" diameter). (A) Optical photograph of a pellet of HKUST-1 MOF compressed at 1,000 psi. Three-dimensional tomography of the pellet also showed good uniformity. However, some small bright spots seen in the pellet via tomography may represent free copper and copper oxide particles (which may ultimately provide a conduit for dielectric break-down). Image (B) shows intensity (arbitrary units) versus diffraction angle θ for a powder X-ray diffraction of HKUST-1 pressed MOF (upper diffraction pattern). This is compared to unpressed powder (lower diffraction pattern) showing crystallinity is largely maintained through processing/pressing. It was found that with enough applied force the crystallinity could ultimately be destroyed.

(1Hz - 10⁴Hz). A parallel plate capacitor structure is being used for these measurements. The electric response of the capacitor is analyzed by electrochemical impedance spectroscopy (EIS) using an equivalent circuit model which includes a parallel capacitor-resistor configuration. The directly-measured capacitance (C_p) is used to calculate the real part of the dielectric constant (ϵ_r'). Moreover, the measured resistance of the resistor portion of the circuit (R_p), is directly related to the current leakage in the capacitor and is thus used to calculate the imaginary part of the dielectric constant (ϵ_r''). The basic relationship between the variables is highlighted in Figure 4. The real and imaginary parts of the dielectric constant define the loss tangent ($\tan \delta = \epsilon_r''/\epsilon_r'$), which is a dielectric parameter that quantifies its inherent dissipation of electromagnetic energy. It will ultimately enable us to estimate the “losses” over a charge/discharge cycle. Different experimental configurations and procedures have been designed and tested in order to perform accurate measurements of dielectric properties. The first approach was based on a capacitor configuration that included two parallel copper blocks separated by a compartment that was then filled with a sample of powder. Measurement reproducibility issues were initially encountered due to problems controlling powder packing and uniformity (granular flow/packing problems). Now, specified weights of powder are pelletized under controlled pressure. Then, a capacitor is formed by placing the material pellet between two metal plates connected to a potentiostat/galvanostat capable of performing the required EIS measurements accurately. Dielectric constants and loss tangents have been measured for several MOFs and MOFs impregnated with polarizable constituents such as ferrocene.

We are also currently designing an electric charge/discharge device (capacitor) capable of being inserted into a high-pressure gas loading system. The device is intended for ultimate use in in situ neutron diffraction experiments to determine precisely how MOF crystals (and related structures) respond as the electric field varies. Such probes will also ultimately allow us to monitor hydrogen adsorption at specific internal sites. Hydrogen bonding sites will be refined from the neutron

FIGURE 4. Schematic of test cell assembly for determining dielectric properties, the equivalent circuit and relationship between key variables.

diffraction data and used to improve the next iteration in materials design.

Conclusions and Future Directions

As this Fiscal Year 2009 new start project completes the first year, the following statements can be made:

- Capacitive storage under electric fields offers a practical means of enhancing hydrogen storage (that can be used in conjunction with manipulation of temperature and storage). The energy used to establish the field can largely be recovered upon discharge (less the dielectric losses, which we will quantify).
- The approach is expected to result in more economical combinations of temperature and pressure in hydrogen storage systems. Higher efficiencies and better control over the charge/discharge dynamics are expected (via proper modulation of the field).

Work in progress includes:

- Completing quantitative demonstration of enhanced hydrogen loading in the presence of an electric field.
- Assess H_2 /substrate compatibility under dielectric breakdown.
- Identifying of best porous frameworks to employ as adsorbent substrates - e.g. MOFs; ZIFs; semiconductor composites.

While this is a materials discover project, we expect to compare measured loadings with On-Board Hydrogen Storage System Technical Targets storage targets as data is obtained, with continuous down-selection of materials for subsequent performance testing in integrated storage systems. This is an ambitious materials design endeavor and it is recognized that there will be practical limits on the applied voltages, e.g. a break-down potential across the dielectric will always be lurking. However, success will define a new, and needed, direction in the stabilization of molecular hydrogen.

Special Recognitions & Awards/Patents Issued

1. A Provisional US Patent Application was prepared and submitted in 2009: “Apparatus and Method for Gas Storage and Separation” Agent Docket Number: S-112,957. R.P. Currier, S.J. Obrey, J.-M. Sansiñena, and D.J. Devlin.

FY 2009 Publications/Presentations

1. “Capacitive Storage of Gases in Porous Dielectric Materials” R.P. Currier, D.J. Devlin, N. Henson, S.J. Obrey, B.M. Patterson, J.-M. Sansiñena (presenter), Q. Wei, Y. Zhao. Presented at the 11th Annual *ELECTRIC POWER Conference & Exhibition*, Chicago, IL May (2009).

2. “Capacitive Hydrogen Storage Systems: Molecular Design of Structured Dielectrics” poster presentation. R.P. Currier, D.J. Devlin, N. Henson, S.J. Obrey, B.M. Patterson, J.-M. Sansinena, Q. Wei, Y. Zhao. Presented at the DOE Hydrogen Program Annual Merit Review and Peer Evaluation Meeting, Washington, May (2009).
3. “Metal-Organic Aerogels: A New Class of Aerogels Composed of Metal Clusters and Organic Ligands” Q. Wei, H. Kim, D. Yang, K.A. Obrey, G. Zou, P. Chupas, Z. Lin, R. Zou, Y. Wang, S.J. Obrey, R.P. Currier, T.E. Proffen, H. Xu and Y. Zhao. Submitted to *Science* (2009).
4. “Kinetic Hysteresis Adsorption Behavior in MOFs with Zig-Zag Channels” Q. Wei, S.J. Obrey, R.P. Currier, H. Xu and Y. Zhao. In Preparation (2009).

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IV.F.3 Hydrogen Storage Materials with Binding Intermediate between Physisorption and Chemisorption

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Contract Number: DE-FG36-5G01004

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Project End Date: September 30, 2010

Objectives

- Synthesize and characterize novel nanoporous hybrid materials with improved affinity for hydrogen.
- Use advanced characterization methods (inelastic neutron scattering spectroscopy, computation, etc.) and thermodynamic data to discern hydrogen binding mechanisms at particular sites.

Technical Barriers

This project addresses the following technical barriers from the Storage section (3.3) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) System Weight and Volume
- (C) Efficiency
- (P) Lack of Understanding of Hydrogen Physisorption and Chemisorption

Technical Targets

The objective of the project is to develop hydrogen storage materials for reversible on-board applications

with hydrogen binding energies intermediate between physisorption and chemisorption. Such materials need to reach a binding energy for hydrogen in the range of 15–25 kJ/mol averaged over all sorption sites.

Accomplishments

- Determined the type of metal site which interacts most strongly with hydrogen by carrying out systematic studies of various types of metal binding sites in zeolites and coordination polymers.
- Investigated intra-framework metal sites in analogs of MOF-74 with Co and Mg substituted for Zn, by inelastic neutron scattering (INS) of the adsorbed H₂, and found Mg to have the strongest interaction among these metals.
- Demonstrated the existence of coordinated molecular hydrogen at an open, and highly accessible metal binding site in Cu-ZSM-5.
- Confirmed evidence for possible binding of two hydrogen molecules at Cu(I) sites in Cu-ZSM-5.
- Completed our investigation of the synthesis of hybrids with a highly functionalized link, 2,5-thiazolo[5,4-*d*]thiazole dicarboxylic acid, and several series of metals, including alkali, alkaline earths and first row transition metals, which did not yield a material with appreciable porosity.
- Synthesized a total of 18 new hybrid metal organic frameworks (MOFs) with fluorine-substituted organic linkers.
- Obtained a new hybrid material with a tetrafluoroterephthalate, zinc, and 1,2-bis(4-pyridyl) ethane with substantial porosity.
- INS studies of H₂ in Zn(1,2,4-triazolate) (tetrafluoroterephthalate) reveal three strong binding sites, with interaction much greater than typical MOFs, and serve to understand the relatively high isosteric heat of adsorption of 8 kJ/mol over a wide range of loadings.

Introduction

The vast majority of hydrogen storage materials currently under consideration fall into either of two categories, those with high surface areas, such as carbons of various kinds, MOF materials and other coordination polymers, which bind hydrogen by weak physisorption, or various light metal hydrides, or other

“chemical hydrides” such as aminoborane, which bind hydrogen very strongly, essentially in the form of a chemical compound. Many sorption-based systems approach sufficiently high capacities at low temperatures and high pressures, but not under ambient conditions, while the hydride compounds have impressive capacities at room temperature but suffer from various problems, such as undesirable H_2 release characteristics, a lack of reversibility, or cyclability, and potential system deactivation.

There is clearly an urgent need to develop another approach to that hydrogen storage materials which would have the potential to provide superior performance especially in those aspects where current systems have serious shortcomings. We believe this to be a system based on sorption, in which the host-guest interactions are intermediate between those found in the carbons and the metal hydrides, i.e. between physisorption and chemisorption. This must be accomplished by combining in one material several attributes that are known to increase the isosteric heat of hydrogen adsorption. These include the creation of open transition metal binding sites, especially if these can bind multiple dihydrogen ligands, modification of the organic linker by substitution of H with Cl or F, for example, the use of charged, rather than neutral frameworks, and materials with small pores. A suitable combination of these elements could well reach the desired goal of a hydrogen binding energies near 20 kJ/mol, which is necessary for operation at room temperature and modest pressures. The following classes of materials are currently under investigation by us:

- i. Hybrid materials with fluorinated organic linkers.
- ii. Materials with open metal binding sites for molecular chemisorption of hydrogen coupled with functionalized linkers, materials with extra framework metal sites introduced post synthesis by various methods, and anionic frameworks with exchangeable cations.

Approach

The primary focus our work has been to improve the binding energies for hydrogen in porous materials into the range of 15–25 kJ/mol needed for a room temperature sorption based storage system given the fact that it has already been demonstrated the necessary surface areas can be achieved. Our synthetic work therefore is aimed at creating novel inorganic-organic framework materials either based on transition metals with the ability to bind more than one molecular hydrogen ligand by molecular chemisorption, and/or the development of hybrids materials that combine a number of strategies, each of which may improve binding energies by some 50% relative to those of standard, neutral MOFs. We are attempting to accomplish this

by one or both innovative methods, namely the use of fluorinated organic linkers, in combination with open metal sites, small pore systems and charged frameworks. The key experimental component in this effort is the use of inelastic neutron scattering of the hindered rotation of the adsorbed H_2 molecule, which makes it possible to associate improvements in binding energies from thermodynamic measurements with specific binding sites. Once a promising material is identified and characterized it will be modified to increase its surface area to achieve capacity goals.

Results

(i) Hybrid materials with fluorinated organic linkers: Because of the fact that we must improve the binding energy of hydrogen in these sorption based systems, we have been developing the synthesis of hybrid organic-inorganic structures using fluorinated organic ligands as linkers. In the course of this effort we have completed a systematic investigation [1] of hybrid materials which possess one fluorinated (terephthalate, isophthalate, succinate, and hydroxybenzoate), and one non-fluorinated linker (4,4'-bipy, and 2,2'-bipy) (Figure 1a) together with a variety of metals (Zn, Mn, Co, and Cu). We were successful in synthesizing a very large number of novel, previously unknown hybrid materials which incorporate fluorinated links, only one of these compounds [2], $Zn_5(C_2H_2N_3)_6(C_8F_4O_4)_2(H_2O) \cdot 2H_2O$, a three-dimensional coordination polymer containing 1,2,4-triazolate and tetrafluoroterephthalate ligands, was found to be porous with a rather modest surface area of 150 m²/g.

We have previously reported [2] that the isosteric heat of adsorption for hydrogen in this material is more than 50% higher than that in a typical MOF (without F substitution), which is now convincingly supported by our very recent inelastic neutron scattering data on this system obtained on the TOFTOF Spectrometer of the FRM-II reactor at the Technical University of Munich, Germany (Figure 1b). The positions of the three peaks in the INS clearly indicate a much stronger interaction in the presence of the fluorinated linker, as all of them occur well below 10 meV unlike those in MOF-5 (all transitions are above 10 meV), or those of several compounds (e.g. HKUST-1) with so-called open metal sites.

Based on our success in synthesizing a large number of novel hybrid materials which incorporate fluorinated carboxylates along with various triazolate and bipyridine ligands, we have now expanded this work to include the larger bipyridine-based ligands in combination with perfluorinated dicarboxylates in order to achieve significant porosity in these materials. We have now synthesized several phases incorporating the ligands 1,2-bis(4-pyridyl)ethane (bpa) and 1,3-bis(4-pyridyl)

FIGURE 1. (a) Ligands used in the synthesis of partially fluorinated hybrids: (top, from left): 1,2,4-triazole, 2,2'-bipyridine, 4,4'-bipyridine; (bottom, from left): F_4 -isophthalate, F_4 -terephthalate, F_4 -succinate, F_4 -hydroxybenzoate; (b) INS spectra of $Zn(1,2,4\text{-triazolate})(\text{tetrafluoroterephthalate})$; (c) $Zn(\text{bis}(4\text{-pyridyl})\text{ethane})(\text{tetrafluoroterephthalate}) \cdot \text{cyclohexanone}$.

propane, the most interesting of which is a structure containing zinc, 1,2-bis(4-pyridyl)ethane and tetrafluoroterephthalate (tftpa) (Figure 1c). We were successful in achieving significant porosity in this system by adding a templating molecule to the reaction. This new structure is a four-fold interpenetrated structure with the large pore filled with cyclohexanone molecules formed regardless of this high degree of interpenetration. The unique lattice is built up from tetrahedrally

coordinated Zn^{2+} centers bound to two bpe ligands and two tftpa ligands. The ligands both act as linear linkers between other metal centers, forming a diamond-like net in three dimensions.

(ii) Materials with open metal binding sites:

We have completed our systematic search for new hybrid materials that are composed of a highly functionalized link, 2,5-thiazolo[5,4-*d*]thiazolecarboxylic acid (Thz) (shown below).

and three series of metal centers, namely transition metals, alkaline earths and alkali metals. These compounds were synthesized under conditions that could also produce removable ligands on the metal and thereby create open metal binding sites. These efforts resulted in a considerable number of interesting new structures that were found to be governed by some well defined trends in the dimensionality of metal-ligand chains and metal polyhedra connectivity, but none of these materials exhibited appreciable porosity. The reason for this was found to be in the nature of the heteroatoms on the organic, which can also coordinate to the metal, and hence produce more compact structures. Materials with the largest metal cations did have more open structures, but this size effect was insufficient to introduce porosity. The most recent example in this series, a three-dimensional framework with cadmium (Figure 2) features two chemically distinct Cd^{II} centers: a pentagonal bipyramid (7-coordinated) and a distorted octahedron (6-coordinated). Chains of $Cd\text{-Thz}$ are connected to form layers with the octahedral Cd^{II} through carboxylate oxygen atoms on axial positions, with potentially removable water molecules occupying the four equatorial positions.

It has become increasingly apparent that the benefit of so-called “open” metal sites in terms of hydrogen binding energies is much more limited than expected, so that the increase in binding energies averages only some 5 kJ/mol relative to MOFs with no such sites. One of the reasons for this is that these sites are not closely accessible to the hydrogen molecule, as has been determined in a few cases by neutron powder diffraction [2]. The formation of a true molecular hydrogen complex with much higher binding energy is thereby prevented.

We have therefore carried out a systematic study of the effect of metal binding sites in porous materials which includes (1) open metal sites that are part of MOFs, (2) extra-framework cations in at various sites in different types of zeolites, and (3) exchangeable, hydrated cations in anionic framework zeolite(-type) MOFs (ZMOF). In the first instance we obtained INS

FIGURE 2. Structure of Cd(2,5-thiazolo[5,4-d]thiazole-5-carboxylic acid): (top) view perpendicular to the plane of the layers. Octahedral Cd^{II} in purple, pentagonal bipyramidal Cd^{II} in gray-blue. Guest water molecules omitted for clarity. (bottom): view along the plane of the layers.

spectra for H₂ in two examples (Figure 3) of the more promising materials among neutral MOFs with open intraframework metal sites, namely analogs of MOF-74, where the metal center can be replaced with a variety of other metals. These CPO-27 type materials M₂(dhtp) (H₂O)₂·8H₂O, (H₄dhtp = 2,5-dihydroxyterephthalic acid, M = Mg, Mn, Co, Ni, Zn) [3-5], have been reported to have hydrogen binding energies well in excess of 10 kJ/mol but only at rather low loadings.

The effect of EXTRA-framework metal ions (as opposed to INTRA-framework), on the other hand is much more pronounced. This is clearly demonstrated clearly by our ongoing work on the Fe- and Cu-ZSM-5 system. We have previously reported [6] that the binding of molecular hydrogen to Cu and Fe in these zeolites is by far the strongest of any porous host material, as much as 70 kJ/mol in Cu-ZSM-5, whereas the INTRA-

FIGURE 3. INS spectra ($T = 5\text{K}$) of Co- (top) and Mg-coordination polymer Oslo (CPO)-27 (bottom) at hydrogen loadings up to one H₂ molecule per metal site.

framework Cu sites in HKUST-1, for example, only gives rise to binding energies in the range of 6-8 kJ/mol. Our computational analysis of these systems (collaboration with Xavier Solans-Montford and Mariona Sodupe Roure of the Universitat Autònoma de Barcelona) unambiguously shows that it is the long-anticipated formation of an actual metal-dihydrogen complex, which results in such strong binding. The metal-dihydrogen coordination in turn is facilitated by the highly open and under coordinated structure of the metal binding site, whereby the Cu ion is bound to just two framework O atoms (Figure 4). In the case of Fe-ZSM-5 we find that the binding site is in fact FeO coordinated to two framework O atoms, and that the interaction with H₂ is much weaker, i.e. 13 kJ/mol. A second H₂ molecule may be bound to the Cu site in ZSM-5, albeit with much lower binding energy. This could, however, be partly responsible for the decrease in isosteric heat of adsorption with increased loading observed by us [6].

FIGURE 4. Theoretical structures of two binding sites in Cu- (left) and Fe-ZSM-5 (right). The site in the six-ring window (top) is much less favorable than the site in the large cavity. Bis-dihydrogen binding at the Cu-site is shown at the bottom.

Our INS studies on various zeolite model systems [7] provide additional evidence for the efficacy of under coordinated extra-framework metal ions in hydrogen binding. The incorporation of Li^+ ions in MOFs is widely considered as crucial for obtaining a low-density material with strong H_2 interactions. INS data obtained on zeolite Li-A, however shows, that only the undercoordinated Li site in the 8-ring window binds H_2 strongly (rotational tunneling transition at ~ 1 meV) whereas the Li site in the six ring window interacts only weakly (~ 8 meV) with the adsorbed hydrogen.

MOF-type porous materials, however, typically have neutral frameworks, which do not lend themselves to simple ion exchange. Our collaboration with the group of Mohamed Eddaoudi (University of South Florida) has included anionic frameworks (ZMOFs) which possess the third type of metal site investigated, namely exchangeable cations in hydrated form. These materials may be viewed as analogues to zeolites with their charged frameworks, and do, in fact exhibit an increase

in binding energy for hydrogen of some 2-3 kJ/mol on account of the electrostatic field in their cavities. The effect of the exchangeable cation, however, does not appear to go much beyond that of the electrostatics, as our INS studies [8] of several forms of this material with different cations show only small differences in hydrogen binding energies. The reason for this is no doubt the fact that the metal cation cannot be closely approached on account of the aquo ligands that surround it.

Conclusions and Future Directions

This project has entered phase II, where the principal emphasis will be on increasing hydrogen binding energies in the most promising materials discovered in phase I based on the results of our investigations described above. More specifically, we aim to achieve post-synthesis introduction of Cu, or Fe (or other metal with high affinity for H_2) into an existing anionic ZMOF with very high surface area in such a way as to create highly under coordinated, open

metal sites. These sites may be expected to be suitable for dihydrogen coordination with the attendant high binding energies. The second, major goal of this phase is to enhance our very promising, partially fluorinated hybrid materials with open metal sites, in addition to other structural enhancements (small pores, anionic frameworks) to achieve hydrogen binding energies well in excess of 10 kJ/mol, along with surface areas exceeding 500 m²/g or greater.

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IV.F.4 Novel Metal Perhydrides for Hydrogen Storage

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Contract Number: DE-FC36-05GO15003

Project Start Date: April 1, 2005
Project End Date: November 11, 2009

Objectives

- The overall focus of this project:
 - Develop new kinds of materials that are able to bind hydrogen molecules into clusters.
 - Enhance hydrogen adsorption/desorption by means of hydrogen cluster formation/decomposition so that the capacity of materials for hydrogen storage and the kinetics for hydrogen release have potential to meet the DOE 2010 and 2015 target.
- The objective for Fiscal Year 2009:
 - Study the H₂ adsorption behavior of material systems having charged species in the material structure.
 - Design and develop material systems capable of auto-charging under H₂ pressure.
 - Study the H₂ adsorption behavior of materials systems capable of auto-charging under H₂ pressure.
- Design and develop devices for directly measuring H₂ sorption in electric field.
- Study the H₂ adsorption behavior of materials systems charged by applied electric potentials.

Technical Barriers

This project addresses the following technical barriers from the Storage section (3.0) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) System Weight and Volume
- (B) System Cost
- (C) Efficiency

Technical Targets

This project is focused on the use of charged species to form H₂ clusters and thus to enhance the H₂ storage capacity. Insights gained from these studies will be applied toward the design and synthesis of hydrogen storage materials and systems that meet the following DOE 2010 hydrogen storage targets, as shown in Table 1:

TABLE 1. DOE 2010 Hydrogen Storage Targets

Storage Parameter	Units	2010
Usable, specific-energy from H ₂	kWh/kg	2
(net useful energy/max system mass)	(kg H ₂ /kg system)	(0.06)
Usable energy density from H ₂	kWh/L	1.5
(net useful energy/max system volume)	(kg H ₂ /L system)	(0.045)

Accomplishments

- Advance the research focus from computer modeling to direct H₂ sorption.
- H₂ sorption on five material systems has been investigated:
 - Dehydrated vermiculite
 - Activated carbon + charge-generating materials (CGMs)
 - NiO + CGM
 - Activated carbon + 2,000 V potential
 - Pt/carbon + activated carbon + 2,000 V potential
- All of the five systems demonstrated enhanced H₂ sorption in the presence of charges.
- Electrically-charged system yields 200 to 550% hydrogen sorption enhancement with spill-over approach at room temperature under 1-5 bar pressure.
- More than 6 wt% hydrogen storage capacity has been reached at 77 K on a material basis.

Introduction

Research on hydrogen storage materials has been pursued for many years, and has proven to be a difficult task. The key problem involved in reversible hydrogen storage materials is perhaps that most of the candidate materials are much heavier than carbon but their capabilities to bind hydrogen (in atomic ratios) are lower. In addition, the host materials cannot contribute to the energy content of the fuel. It becomes more and more apparent that hydrogen storage could not solely rely on surface properties of host materials. Additional attracting forces have to be introduced.

This project is to develop novel materials that use charged species to cluster hydrogen in the material structures. The clustering approach is anticipated to lead to higher hydrogen uptake than that obtained by means of conventional chemical and physical sorption. On the other hand, the charged species may affect the electronic structure of the host materials and therefore enhance the attraction of hydrogen to their surfaces. The novel materials are anticipated to uptake sufficient amounts of hydrogen and are promising for meeting the DOE 2010 and 2015 targets.

Approach

The proposed charge-induced hydrogen clusters include proton-hydrogen clusters, $[H(H_2)_n]^+$; cation-hydrogen clusters, $[M(H_2)_n]^{z+}$; anion-hydrogen clusters, $[X(H_2)_n]^{z-}$; clusters around polar chemical bonds, $\delta^+[(H_2)_m M-X(H_2)_n] \delta^-$; and clusters that may form on electrodes, anode- $(H_2)_n^{q+}$ - $(H_2)_n^{q-}$ -cathode. Based on the charge cluster concept, we anticipated that the hydrogen sorption on sorbent materials would be enhanced if an electric field is applied.

In this year's research, we employed two approaches to introduce the electric field: directly applying an electric potential to the sorbent materials, and burying a piezoelectric element inside the sorbent materials, which could autogenously generate electric charges under hydrogen pressure. Direct measurement of hydrogen sorption under electric field was carried out with PCTPro-2000. A special sorption reactor has been developed to interface with PCTPro-2000 for carrying out the sorption experiment

Results

Our experimental results revealed that applying an electric potential to pure carbon did result in enhanced hydrogen sorption on the material. It supports our initial assumption. It was further found that the sorption enhancement could be appreciably

promoted when platinum was present. As illustrated in Figure 1, enhancement of fivefold on Pt-supported carbon could be reached under lower hydrogen pressures. It is well known that the presence of platinum could induce spillover sorption of hydrogen. By the spillover mechanism, hydrogen molecules dissociate into hydrogen atoms that diffuse toward sorption sites via low energy paths. From our own observations, we conclude that applying an electric field could make the spillover sorption more effective.

Figures 2 and 3 show the sorption curves obtained from our experiment of hydrogen sorption on carbon and NiO samples in the presence of a piezoelectric

FIGURE 1. Hydrogen Sorption on Pt-Supported Carbon with and without Electric Field

FIGURE 2. Hydrogen Sorption on Carbon in Presence and Absence of Electric Field

FIGURE 3. Hydrogen Sorption on NiO in Presence and Absence of Electric Field

element, respectively. It is obvious that on both samples, the presence of the piezoelectric element increased the hydrogen sorption. Once again, this verified our concept that electrical charges could have stronger forces to bind hydrogen. The sorption enhancement trends illustrated by the sorption curves are consistent with the charge-generating capability of the piezoelectric elements. Under higher hydrogen pressure, stresses in the piezoelectric element would become more intensified. More electrical charges could be generated at the surface of the piezoelectric elements.

It is interesting to note that in the case of NiO, the enhancement appeared to be more distinctive in the low pressure range and more significant in the high pressure range, compared to that of the carbon samples. The greater enhancement of sorption on NiO is attributed the catalytic characteristics of NiO. Similar to Pt-supported carbon, the nickel species could split hydrogen molecules into hydrogen atoms and make the electric field-induced enhancement more effective.

The accomplishment on electric field-induced sorption enhancement has led our efforts to address structure characteristics of the sorbent materials. Besides the catalytic species, we have investigated other measures to improve the accessibility of charges in the sorbent structure. A special material, termed a structure modifier, was found that could dramatically increase the hydrogen uptake of carbonaceous materials. Figure 4 illustrates the sorption curves of a pure carbon (C), carbon + piezoelectric element, and carbon + piezoelectric element + structure modifier. The result demonstrated that, in electric field, the 77 K hydrogen uptake capacity of structure modified carbon exceeded the target of 6.0 wt%.

FIGURE 4. Effect of Electric Field and Structure Modifier on Hydrogen Sorption at 77 K

Conclusions and Future Directions

The criterion for the Go/No-Go decision of the MTU project is “The decision to go forward to Phase II will be based on the demonstration of at least 6 wt% hydrogen storage capacity (on a material basis) for at least one of the metal perhydride materials developed in Phase I”. The MTU Phase I project has been able to achieve more than 6 wt% hydrogen storage capacities at 77 K on a material basis so far. It is predicted that a significant improvement over the 6 wt% hydrogen sorption capacity will be realized in the Phase II study since the fundamentals of the perhydride has been well established in the Phase I study. In Phase II, we will optimize the sorbent materials and the storage system structures. The combination of the optimized material and system structures would be able to hold a high population of electric charges and therefore perhydride species of high density could be produced. Approaches for harvesting the electrical charges during the hydrogen release cycle will also be developed, so that the hydrogen storage system could act concurrently as a battery. The overall energy storage capacity could be further increased.

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IV.F.5 Electron Charged Graphite-Based Hydrogen Storage Material

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Contract Number: DE-FG36-05GO15010

Subcontractor:

Superior Graphite Co., Chicago, IL

Start Date: July 1, 2005

Projected End Date: September 30, 2010

Objectives

- Preparation of high surface area carbon-based materials and generation of small particles to allow access for hydrogen adsorption.
- Electron-rich material doping into high surface area carbon to increase electron charges onto/into the carbon, so the hydrogen adsorption becomes combined physisorption and chemisorption.
- Addition of electron charge during hydrogen filling to increase hydrogen storage with discharge to release hydrogen.

Technical Barriers

This project addresses the following technical barriers from the Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) System Weight and Volume
- (B) System Cost
- (C) Efficiency
- (D) Durability/Operability
- (E) Charging/Discharging Rates
- (Q) Reproducibility of Performance

Technical Targets

This project involves conducting research on graphite-based materials for hydrogen storage with external electronic charges to increase hydrogen storage capacities and charge/discharge rates that meet the following DOE 2010 hydrogen storage targets:

- System Gravimetric Capacity: 0.045 kg H₂/kg system
- System Volumetric Capacity: 0.028 kg H₂/L system
- Durability/Operability: 1,000 cycles
- Cost: \$4/kWh net

Table 1 shows progress toward meeting the DOE on-board hydrogen storage targets.

TABLE 1. Progress Toward Meeting DOE On-Board Hydrogen Storage Targets

Storage Parameter	Units	2010 System Target	FY09 system*
System Gravimetric Capacity	kg H ₂ /kg system	0.045	0.028
System Volumetric Capacity	kg H ₂ /L system	0.028	0.101
Storage System Cost	\$/kg H ₂	133	>1200
Adsorption/desorption Temperature	°C	-30/50	-20/120

*GTI metal hydride-based material (3 wt% hydrogen storage) with tank at 1,000 psi

Accomplishments

- Worked with partners to explore high surface carbon (AX-21 and other high surface area carbons) for hydrogen storage with the help of electrostatic charges.
- Repeated the electron charge effect experiments on the hydrogen storage capacity of materials and conclude that positive charge increases hydrogen storage on metal-based material and negative charge increases hydrogen storage on non-metal hydrogen storage materials.
- Tested the external charge effect on the hydrogen charge/discharge kinetics, especially on-site regeneration of borane-nitride materials.
- Designed a practical 11-liter hydrogen storage charge system with electron-charge and cooling/heating for hydrogen uptake and release. The system hydrogen storage capacity is 0.028 kg H₂/kg system and 0.101 kg/liter system.

Introduction

Hydrogen adsorption on metal-based materials suffers slow kinetics for hydrogen uptake and release with storage gravimetric capacity 3.3 wt% at material base. Hydrogen molecules are physisorbed on carbon-based materials at temperatures as low as 77 K. The metal-based materials are polar substrates while the carbon materials are non-polar substrates. The non-polar hydrogen molecules adsorbed on a non-polar carbon substrate are not dissociated and the force between these two non-polar species is basically the weak van der Waals force. The non-polar hydrogen molecules adsorbed on a polar (metal) substrate generate an electron spillover effect. Whatever the substrate is, polar or non-polar, the external electrical force could polarize the substrate surface to change the hydrogen adsorption capacity and kinetics.

Approach

- Test and evaluate cycles for hydrogen storage:
 - Modify the electron charge distribution structure (framework structure) to obtain a 50% hydrogen storage rate increase.
 - Fueling kinetics study: does the electron charge make desorption fast?
 - Theoretical calculation: how much charge is needed to get 6 wt%?
- Optimize charge control agent (CCA) and charge transfer agent (CTA) to help polarize storage materials.
- Characterize the electron device and the material properties of the carbon-based material with CCA/CTA (pore size, density, surface area, etc).
- Scale-up to an 11-liter tank for fueling demonstration to show 50% hydrogen storage increase.

Results

A. Hydrogen Storage Tests with/without Electrostatic Charge

1. System Design

The external electron-charge has been demonstrated to have an effect on the hydrogen storage kinetics and capacities. Figure 1 displays the design of an electron-charged hydrogen storage system (11-liter tank). In this system, a stainless steel coil with polymer coating insulation is inserted into the tank. The functions of the stainless steel coil are conducting electron-charge and cooling/heating the hydrogen storage materials.

FIGURE 1. Electron-Charged Hydrogen Storage System Design

A similar 10 ml system is used for material screening and hydrogen storage tests.

2. Hydrogen Storage Tests

The electron-charge hydrogen storage system has been scanned to check for any internal short under hydrogen storage pressure and found that even if the voltage goes to 1,000 volts, the leak current is very small as tested in the milli-ampere scale. Therefore all the tests using this system show the electro-static non-Faradaic effect on the hydrogen storage.

A metal-modified AX-21 carbon mixed with CCA was used to test the electron-charge effect on hydrogen storage. Figure 2 exhibits the external electron-charge effect on the hydrogen storage pressure concentration isotherm curves. At room temperature, positive charge increased adsorption on the metal modified AX-21.

Borane-nitride is a very attractive material for hydrogen storage. Its hydrogen storage capacity is theoretically more than 10 wt%. However, the hydrogenation and dehydrogenation kinetics are too slow. At 80°C, the hydrogen release takes more than 24 hours to release 5.70 wt%.

At 900 psi, the decomposition of borane-nitride for 1.5 wt% takes 2.5 hours without electrical charge and only 40 minutes with negative charge as shown in Figure 3. The decomposition rate under electrical charge at different pressures will be generated. Figure 4 shows the electrostatic effect on hydrogen storage with 1.00 g borane-nitride and 0.05 g catalyst at 80°C. The threshold point occurs when pressure increases to 6 MPa with negative charge. These results once again verified that negative charge increases the hydrogen storage again.

B. High Surface Carbon for Hydrogen Storage

The cooperation with State University of New York (SUNY) at Syracuse helps us to develop the hydrogen storage electron-charge system. GTI tested eight samples

FIGURE 2. Electro-Static Voltage Effect on Hydrogen Storage at Room Temperature

FIGURE 3. Electro-Static Voltage Effect on Hydrogen Release of Borane-Nitride at 80°C and 900 psi H_2 Pressure

FIGURE 4. Electro-Static Voltage Effect on Hydrogen Storage Material B-N at Room Temperature

and the results are summarized in Table 2. The best hydrogen storage gravimetric capacity is 7.0 wt% at 77 K.

TABLE 2. Summary of SUNY samples at 6,300 kPa

Sample name	0°C (wt%)	77 K (wt%)
APPANNI(2)	0.52	6.5
APKI6S2	0.40	7.0
MK775	0.44	5.8
PK-NaH-1-1	0.38	4.4
APTPN1	0.49	6.4
N24Ma1045	0.33	4.8
N24	0.52	7.0
APK25N1	0.77	6.0

Conclusions and Future Directions

- The electron charge effect experiments on the hydrogen storage capacity of materials conclude that positive charge increases hydrogen storage on metal-based material and negative charge increases hydrogen storage on non-metal hydrogen storage materials.
- The external charge shows the effects on the hydrogen charge/discharge kinetics, especially on-site regeneration of borane-nitride materials – 75% increase at 600 psig.
- A practical 11-liter hydrogen storage charge system with electron-charge and cooling/heating for hydrogen uptake and release was designed. The system hydrogen storage capacity is 0.028 kg H_2 /kg system and 0.101 kg/liter system.
- Test 11-liter hydrogen storage system for practical applications.

FY 2009 Publications/Presentations

- A poster presentation regarding the overall project status was given at the DOE Annual Merit Review Meeting (May 20, 2009).

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IV.G.1 Compact (L)H₂ Storage with Extended Dormancy in Cryogenic Pressure Vessels

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Start Date: October 1, 2004
Projected End Date: September 30, 2011

Objectives

- Build and test cryogenic pressure vessels.
- Demonstrate cryogenic vessel onboard a vehicle.
- Test thermal endurance and heat transfer rate.
- Test composite vessel outgassing and vacuum stability.
- Test vessel cycle life at liquid hydrogen (LH₂) temperature and high pressure.
- Test para-ortho and ortho-para conversion at cryogenic temperatures.

Technical Barriers

This project addresses the following technical barriers from the Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) Weight and Volume
- (D) Durability
- (H) Balance of Plant (BOP) Components
- (O) Hydrogen Boil-Off

TABLE 1. Progress toward Meeting DOE On-Board Hydrogen Storage Technical Targets

Lawrence Livermore Cryo-Compressed Vessels					
Storage Parameter	Units	2010 Target	2015 Target	2007, 2 nd generation [§]	2009, 3 rd generation*
Specific Energy	kWh/kg	1.5	1.8	1.8	2.31
Energy Density	kWh/L	0.9	1.3	1.04	1.42
Storage System Cost	\$/kWh	4	2	13.6	13.6

[§] From Argonne and TIAx [1,2]

* Preliminary estimates being certified by independent analysis

Accomplishments

- Demonstrated generation 3 cryogenic pressure vessel that stores hydrogen at 45 gH₂/L and 7.5% H₂ weight fraction, thereby meeting the DOE 2015 targets.
- Conducted vacuum stability tests and chemically analyzed composite outgassing.
- Designed experiment for cryogenic cycle test.
- Designed experiment for para-ortho conversion.

Introduction

As a universal transportation fuel that can be generated from water and any energy source, hydrogen (H₂) is a leading candidate to supplant petroleum with the potential to ultimately eliminate petroleum dependence, associated air pollutants and greenhouse gases. The predominant technical barrier limiting widespread use of hydrogen automobiles is storing enough hydrogen fuel onboard to achieve sufficient (500+ kilometers) driving range in a compact, lightweight, rapidly refuelable, and cost-effective system. Cryogenic pressure vessels may contribute to solving this challenge. In collaboration with industry, we are currently addressing the remaining hurdles to enable future commercialization.

Approach

Cryogenic pressure vessels being developed at LLNL have potential for enabling practical range through a combination of dense hydrogen storage (LH₂) and efficient packaging density. Cryogenic pressure vessels can store LH₂ with dramatically improved thermal endurance – the main challenge facing conventional

low-pressure LH₂ tanks. Cryogenic pressure vessels have reduced sensitivity to heat transfer and can therefore operate with reduced insulation thickness (~1.5 cm vs. ~3 cm for low-pressure LH₂ tanks), considerably improving packaging efficiency leading to vessels that meet DOE's 2015 weight and volume targets and approach DOE's ultimate weight target. Current work focuses on improving the technology through innovative designs, collaboration with industry, and system performance experiments.

Results

Cryogenic vessels often demand thick insulation (~3 cm) for adequate thermal performance, negatively impacting volumetric hydrogen storage capacity. Thermodynamic analysis and experiments [3] indicate that cryogenic capable pressure vessels are approximately an order of magnitude less sensitive to heat transfer than conventional low-pressure cryogenic systems, thus enabling thin thermal insulation (~1.5 cm) and hence much improved storage density.

Starting with the LLNL generation 2 design [3] and reducing thermal insulation thickness from ~3 cm to ~1.5 cm leads to the LLNL generation 3 design (Figure 1) that is 23% more compact (225 liters vs. 297 liters), meeting the very challenging DOE 2015 weight and volume targets. Ultra-thin insulation may suffice for controlling heat entry at ~5-7 Watts through careful vessel support and insulation design, maintaining ~3-5 days dormancy for a full tank and avoiding evaporative losses under typical utilization scenarios. Dormancy will increase rapidly as the vehicle is driven and the fill level drops.

Aside from vessel fabrication, we are conducting experiments to test critical performance issues that

FIGURE 1. Generation 2 (left) and generation 3 (right) cryogenic pressure vessels. Generation 3 vessel is 23% more compact through reduced insulation thickness (1.5 cm vs. 3 cm).

may limit commercialization. Vacuum stability is a key feature. Excessive outgassing from the composite vessel may degrade the insulation performance and drastically reduce dormancy. We are therefore testing the outgassing behavior of composite pressure vessels by storing them inside a steel vacuum chamber at specified temperatures (20, 60 and 80°C). We are testing four small-scale (~1 liter) composite pressure vessels with aluminum lining and carbon fiber reinforcement. The vessels have four different surface and curing treatments: 1) regular pressure vessel with no special surface treatment; 2) vacuum cured pressure vessel; 3) ultraviolet (UV) protection coated pressure vessel; and 4) vacuum cured and UV protection coated pressure vessel. The pressure vessels are placed one at a time inside the vacuum chamber that is connected to a vacuum pump (Figure 2). The amount and composition of outgassing from the composite vessel at the different temperatures are measured while keeping a high vacuum. This experiment has the purpose of identifying surface treatments that may reduce outgassing. Identifying the amount and composition of the outgassing will enable optimum selection of absorbent (getter) materials that will maintain high insulation performance in a commercial cryogenic pressure vessel.

The experiments are in progress and have identified detailed outgassing composition including a large family of hydrocarbons in the range of a few to 100 parts per billion. The main hydrocarbon species for the regular vessel (no surface treatment) have remained consistent between experiments at different temperatures, although vessels with other surface treatments are yet to be analyzed. Water is the main component of outgassed samples, and its concentration can be greatly reduced by baking. Hydrocarbons, however, are produced by the vessel even after baking.

Successful commercialization of cryogenic pressure vessels demands cycle life testing. Composite wrapped pressure vessels are typically not designed for cryogenic operation, and fatigue failure may result during repeated cycling. We have therefore proposed a cycle test procedure to address the need for validating composite pressure vessel endurance when pressure cycled at cryogenic temperature (Figure 3). The proposed test includes three operating points identified as most critical for cryogenic vessel operation: minimum temperature (20 K) and low pressure (point 2 in Figure 3), maximum working pressure at low temperature (point 3), and maximum working pressure at below ambient temperature (point 10). We estimate that the overall cycle can be efficiently conducted in ~3 hours when heating the vessel by circulating warm hydrogen (or helium) through the in-tank heat exchanger (2-5 kW depending on vessel temperature). We are planning to repeat the test cycle 300 times.

Finally, we have defined an experimental sequence to test the conversion between the para and ortho

FIGURE 2. Schematic of experimental system for characterization of composite pressure vessel outgassing. The composite vessel is located inside a vacuum vessel, which is then positioned inside an oven for elevated temperature testing.

FIGURE 3. Experimental cycle test for cryogenic pressure vessel consisting of multiple steps: LH_2 fill (points 1-2), cryogenic pressurization by heat transfer (points 2-3), equilibration (points 3-4), depressurization by venting (points 4-5), second pressurization by heat transfer (points 5-6), and equilibration (points 6-7), second depressurization by venting (points 7-8), final pressurization by heat transfer (points 8-9), equilibration (points 9-10), and depressurization to ambient pressure (points 10-11).

states of nuclear spin of the hydrogen molecule. This is important because there is a potential synergy between cryogenic pressure vessels and the conversion of para-hydrogen into ortho-hydrogen as the vessel warms up: para-ortho conversion absorbs energy (because ortho is the higher energy form) and therefore increases the thermal endurance of the cryogenic vessel. This effect is present when most needed: for a nearly full vessel where para-ortho conversion may double the thermal

FIGURE 4. Possible effect of para-ortho conversion in cryogenic pressure vessel pressurization, assuming a pressure vessel initially filled with 8.57 kg of LH_2 (80% fill level) at ambient pressure with 7 Watts environmental heat transfer rate. The figure shows three lines: (1) pressurization neglecting vessel thermal mass and para-ortho conversion (blue), (2) pressurization neglecting para-ortho conversion and including vessel thermal mass (red), and (3) pressurization including vessel thermal mass and assuming phase equilibrium between para and ortho hydrogen phases (purple). Actual pressurization experiment will yield a line between the red and purple lines due to partial (kinetics-limited) para-ortho conversion.

endurance of the vessel if the conversion process is fast relative to the warming process so that the composition remains near phase equilibrium (Figure 4). However, kinetics of conversion from *para* to *ortho* is not well characterized for the broad temperature and pressure ranges in cryogenic pressure vessel operation. Our sequence of experiments will allow us to estimate

the rate of para-ortho conversion at the conditions typically found in a cryogenic pressure vessel as it warms from 20 K (where the equilibrium concentration is approximately 100% para-hydrogen) to 200 K (where equilibrium concentration is near the ambient temperature mixture of 75% ortho and 25% para). Para-ortho conversion can be calculated from thermodynamic analysis of the pressure and temperature data collected as the tank warms up. Comparison with a helium warm-up test will allow for benchmarking and improved conversion estimation.

Conclusions and Future Directions

- Cryogenic pressure vessels can exceed 2015 DOE storage targets for weight and volume, with promising dormancy and cost relative to conventional LH₂ tanks and ambient pressure vessels.
- In collaboration with industrial partners, we are addressing interactions between pressure, temperature, and materials by conducting outgassing, cryogenic cycling, and cryogenic burst tests experiments.
- We are investigating fundamental operational aspects at full scale: internal heat exchange, dormancy and dormancy recovery, para-ortho conversion, and higher density (pressurized) refueling.
- Safety advantages of cryogenic pressure vessels are yet to be assessed. Possible advantages may originate from very low burst energy, fill vs. dormancy safety factor, protective vacuum jacket, and material strength at cryogenic temperatures.

FY 2009 Publications/Presentations

1. High Density Hydrogen Storage in Cryogenic Capable Pressure vessels, Salvador Aceves, Invited presentation, Purdue Hydrogen Symposium, April 2009.
2. Hydrogen-Fueled Carbon-Free Transportation, Salvador Aceves, Invited Presentation, Engineering Solutions for Sustainable Development: Materials and Resources, an international workshop organized by AIME and ASCE, Lausanne, Switzerland, July 22–24.

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IV.G.2 Lifecycle Verification of Polymeric Storage Liners

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Projected End Date: Project continuation and
direction determined annually by DOE

test stand to provide rapid thermal cycling between -40 and 125°C by adding a low-temperature chiller with continuously circulated low-temperature refrigerant and by replacing the heater controller to provide thermal cycling control.

- Developed a novel technique for sealing polymer samples against high-pressure hydrogen at subzero temperatures.

Introduction

The objective of this task is to perform durability qualification measurements on specimens of high-pressure storage tank liners. Modern high-pressure hydrogen storage tanks use a polymeric liner as a permeation barrier, typically high-density polyethylene (HDPE). Storage tank liners can, however, be stressed by cyclical excursions between temperature extremes, and the cumulative effects of repeated stress could harm the tank's durability. Ultra-high environmental temperatures can promote large hydrogen permeation rates and hydrogen saturation in the liner material. Ultra-low environmental temperatures can severely stress liner materials and possibly induce microcracking. In addition, increasing the pressure of gas in such a tank during filling necessarily raises the temperature of the gas and therefore the enclosing tank. Over the course of many fill cycles during the lifetime of the tank this might affect the permeability characteristics of the liner. Failure modes for the liner's performance—based on the interaction of high pressure and extreme temperature cycling—might be possible. Hydrogen leakage through a liner microcracked by extreme temperature cycling could accelerate under sustained high temperature and pressure, or hydrogen saturation of the reinforcement layers external to the liner could put backpressure on the liner as the tank pressure decreases during vehicle operation, thereby causing the liner to separate from the reinforcement layers. Minimum temperatures during winter months in northern states may reach -40°C, and maximum temperatures after filling during summer months may reach 125°C. Thus, the purpose of this project is to cycle typical tank liner materials between these temperature extremes to determine whether such a degradation in properties occurs, and, if so, its extent.

Approach

Hydrogen permeation verification measurements for storage tank liner materials are being carried out using ORNL's IHPV, shown in Figure 1. The IHPV can be used for semi-automatic hydrogen diffusion

Objectives

- Perform durability qualification measurements on specimens of high-pressure storage tank liners.

Technical Barriers

The project addresses the following technical barriers from the Hydrogen Storage section (3.2.4) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

(D) Durability/Operability

Technical Targets

This task addresses the following technical targets for on-board hydrogen storage systems research and development:

- Cycle life variation, expressed as % of mean (min) at % confidence:
 - Fiscal Year 2010: 90/90
 - FY 2015: 99/90
- Environmental Health and Safety:
 - Permeation and leakage: Meets or exceeds applicable standards
 - Loss of usable H₂ (g/h/kg H₂ stored): FY 2010: 0.1; FY 2015: 0.05

Accomplishments

- Modified the ORNL internally heated high-pressure vessel (IHPV) diffusion/permeation measurements

FIGURE 1. IHPV modified to provide rapid cycling between temperature extremes of -40°C to 125°C at differential pressures across the specimen of up to 86 kPa. The photograph shows the specimen loading and permeation measuring end of the IHPV.

and permeation measurements at temperatures over the range 10 to $1,000^{\circ}\text{C}$ and at pressures as large as 276 MPa (40,000 psi). This apparatus has also supported the hydrogen delivery program in determining real-time hydrogen permeation in low-carbon steels and polymer materials. Materials characteristics such as the temperature- and pressure-dependent hydrogen solubilities, diffusion coefficients and permeation coefficients are extracted from measurements of real-time hydrogen flux through steels and polymers.

We are using the relevant portion of the test protocol specified in Society of Automotive Engineers J2579 to guide our performance of durability test cycling measurements of high-pressure polymeric tank liners. The J2579 test protocol for compressed hydrogen storage systems prescribes long-term thermal cycling at high pressures of hydrogen. The requirement is to subject tank liner specimens to 5,500 thermal cycles over the temperature range -40 to 125°C at hydrogen pressurizations of 43 MPa (6,250 psia) and then 86 MPa (12,500 psia). Testing at 43 and 86 MPa, with rapid cycling between -40 and 125°C , requires an automated temperature control strategy. To replicate the rapid temperature rise in the tank liner during fill cycles (approximately 100°C temperature rise in 3 minutes), required us to decouple the cooling and heating control systems in the IHPV. A low-temperature chiller with low-temperature refrigerant circulated to and from a sealed reservoir cools the IHPV's exterior containment vessel to approximately -50°C . A resistive heater situated in the permeation cell is used to ramp the specimen temperature from -40°C to 125°C . A heater controller controls the thermal cycling of the polymer specimen in the cell by applying and removing power to the heater. Process control software that was developed for the temperature-controlled permeation

measurements in steels and polymers was modified to provide automated, unattended operation and Internet access so the tests can be remotely monitored and controlled.

The verification measurements occur at regular intervals during the 5,500 temperature cycles. The hydrogen flux is to be measured at three temperatures (-40 , 25 and 125°C) at each interval, if practicable. The first measurements occur after the completion of 250, 500, 750, 1,000, 1,250 and 1,500 cycles. The remaining measurements occur at 500-cycle intervals until 5,500 temperature cycles have been reached. A second verification test on a fresh tank liner specimen will be carried out at 86 kPa following the same protocol.

Results

We developed a new technique for sealing a thin (0.5 mm) polymer sample against high-pressure hydrogen at subzero temperatures. The sealing method is illustrated in Figure 2. The high-pressure hydrogen is incident against the upper surface of the polymer sample. At subzero temperatures the polymer shrinks (thins) and loses firm mechanical contact with the conical copper sealing ring. We found that it is possible to alleviate this contact loss by pre-forming the polymer to have a conical shape similar to the sealing ring. This was done by placing the polymer specimen against a previously tested (and formed) steel specimen, and then tightening the sandwiched polymer and steel specimens in the specimen holder to force the polymer specimen to acquire a conical contour at its edges without deforming the specimen thickness. The sandwiched specimens were then removed and replaced by the polymer specimen alone.

Initial verification measurements involving 1,500-plus temperature cycles at 43 MPa hydrogen pressure will be completed during last quarter of FY 2009. These initial measurements are being carried out on an HDPE specimen provided by Lincoln Composites. The specimen is being cycled between -40 and 125°C approximately once per hour.

Conclusions and Future Directions

- Perform verification measurements on Quantum Technologies high-pressure tank liner materials.
- Perform verification measurements on pipeline-grade polyphenylene sulfide (ORNL has demonstrated that it has lower hydrogen permeation than HDPE at all temperatures), polyamide 6 (Air Liquide has demonstrated that the permeation of this material is 10x lower than HDPE), and/or polyamide 11 (Arkema is in the process of obtaining approval for use of PA-11 in unreinforced natural gas pipelines).

FIGURE 2. Illustration of method developed for sealing polymer specimen against high-pressure hydrogen at subzero temperatures.

FY 2009 Publications/Presentations

1. 2009 DOE Hydrogen Program Annual Merit Review – Arlington, Virginia – May 19, 2009. Presentation STP01.

References

1. HFCIT MYRDD Plan, Table 3.3.2, "Technical Targets: On-Board Hydrogen Storage Systems," October 2007.
2. SAE J2579, "Technical Information Report for Fuel Cell and Other Hydrogen Vehicles (January 2009)," Fuel Cell Standards Committee, SAE International.

IV.G.3 Low-Cost, High-Efficiency, High-Pressure Hydrogen Storage

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Contract Number: DE-FC36-04GO14010

Project Start Date: July 2008

Project End Date: January 31, 2010

Objectives

This project is to improve the system weight and cost efficiency of Type IV hydrogen gas storage vessels through:

- Liner material and molding process development to reduce liner thickness by 90%, improve production efficiency from approximately 2-hour cycle time to 2 minutes, and reduce the amount of composite usage by roughly 3% in the current pressure vessel (named “129 Liter” used in this project).
- Hydrogen compatible materials study and metal fitting redesign to reduce metal fitting material cost by 80%.
- Liner-metal fitting interface study for proper seal against pressure up to 87.5 MPa.
- Composite manufacturing process evaluation to improve composite reinforcing efficiency and reduce composite usage by 25% in the current pressure vessel.

Technical Barriers

The project addresses the following technical barriers from the Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) System Weight and Volume
- (B) System Cost

Technical Targets

This project is to develop blow molding for liner production and reduce liner thickness; reduce metal fitting material usage and change current material to cheaper hydrogen compatible metals; and optimize current filament winding process to reduce composite material usage. If successful, the project will help to improve the storage efficiency of our hydrogen storage systems towards meeting the DOE target, as listed in Table 1. Quantum has made a lot of such commercially available systems. In Table 1, Quantum’s status is calculated based on a system, which includes a single 129 liter type IV H₂ tank (approximately 5 kg hydrogen capacity at 70 MPa service pressure) with a solenoid valve, a set of high-pressure and low-pressure regulators, a mid stage valve, a receptacle with filter, all tubing and fittings for this system, a frame, a wire harness, a pressure sensor and a balance of parts (consisting mainly of fasteners etc). The end-user cost efficiency is calculated based on an assumption of 500,000 units/year, as well as that 1 kg hydrogen is able to generate 33.3 kWh energy. Per the DOE request, we performed a cost analysis for 10,000, 100,000 and 500,000 units/year. The cost efficiency is approximately \$54.1/kWh and \$48.1/kWh for the first two cases respectively, with the last case shown below in Table 1.

TABLE 1. Progress towards Meeting Technical Targets for On-Board Hydrogen Storage for Light-Duty Vehicles

Storage parameters	Units	2010	Quantum Status
System Gravimetric Capacity	kWh/kg	1.5	1.50
System Volumetric Capacity	kWh/l	0.9	0.83
System Cost	\$/kWh	4	45.9

Accomplishments

- Through material study, we found the right candidate materials to use for the liner blow molding process, and evaluated blow molded liners.
- Finished literature review on hydrogen compatible metals, and selected the candidate material to use to replace current expensive materials in metal fittings.
- Improved the filament winding process and composite reinforcing efficiency through design, 90% finished.

Introduction

The goal of this project is to lower the hydrogen storage system weight and cost of type IV pressure vessels through three different routes. The first is to develop a blow molding process of liner production for liner thickness reduction, more precise quality control and much shorter production cycle time. Quantum has located candidate materials with much better barrier performance than what is currently used, developed a blow molding process, evaluated the liners made through the blow molding process, and demonstrated the feasibility of the blow molding process. The second is to reduce metal fitting material usage by metal fitting design. Quantum has located a much cheaper material to replace the current expensive metal fitting material, and is working to reduce the current metal fitting volume and remove some components. We have made prototypes of the liner-metal fitting interface and proved the feasibility. The third is to improve the filament winding process and composite design to improve composite reinforcing efficiency in the pressure vessel structure. We have improved the translation efficiency (composite reinforcing efficiency) from 65% to 82%.

We plan to continue to work on these three areas and further improve the system cost and weight efficiency.

Approach

Type IV pressure vessels consist of a polymer liner material as the gas barrier, metal fitting for connection to the valve systems, and a fiber reinforced polymer composite to support the load. In the pressure vessel, composite weight is about 90%; composite material cost is about 65% and the metal fitting is about 34% of the vessel. Therefore in order to improve the vessel cost and weight efficiency, we need to work mainly on both composite and metal fittings.

Currently the liner made through rotational molding using high density polyethylene (HDPE) material has a thickness about 5 mm. We are developing a blow molding process to reduce the liner thickness, so that composite usage can be reduced; to improve liner quality control; and to reduce the production cycle time to meet the DOE goal of 500,000 units per year. We are working on a metal fitting design to lower the metal fitting cost by removing component usage, reducing part volume, and changing to cheaper hydrogen compatible materials. We are also working on composite optimization to save composite material usage by improving the filament winding process and composite design efficiency.

Results

Since the project started in July 2008, through thorough material literature study and characterizations, we have successfully located liner candidate materials

which have much better barrier performance than the HDPE liners we currently use. We developed a blow molding process for these materials, and evaluated some blow molded liners. The blow molded polyethylene terephthalate (PET) liners with only 1 mm averaged thickness have a barrier performance about 5 times better than our current 5 mm thick HDPE liners. And the PET liners have passed the ambient pressure cycle fatigue test according to European Integrated Hydrogen Project (EIHP) standards. We also demonstrated the excellent toughness of the liner. Once we can prove the liner-metal fitting seal design, we will demonstrate the feasibility of the blow molding process for liner production. We will evaluate polyethylene naphthalate (PEN) blow-molded liners. We plan to continue to work on this area if we can continue to get funding support. If successful in achieving what we described in the Objectives, the estimated improvement will be from \$45.9/kWh to \$44.9/kWh for the system we discussed before. And the system weight efficiency will be improved approximately from 1.50 kWh/kg to 1.54 kWh/kg. In addition, the success of the blow molding application in liner production will reduce the liner production cycle time from approximately 2 hours to 2 minutes, and help to meet the DOE mass production goal of 500,000 units per year.

We did a thorough literature review and found a few hydrogen compatible metals much cheaper than the material we currently use for the metal fittings. We plan to use these materials to replace the expensive material in the metal fitting. The metal fittings used in the vessel consist of polar boss and adapter. We plan to remove the adapter so that the valve is directly sealed against the polar boss. We also plan to reduce the size of the current polar boss and make it much smaller. We have made prototyped metal fittings according to the new design, and demonstrated the validity of the liner-metal fitting interface seal. We will make new metal fittings using an aluminum alloy and evaluate them according to EIHP tests. If successful in achieving what we have in the Objectives, we will improve the hydrogen storage cost efficiency from \$45.9/kWh to \$44.9/kWh. With continuous funding, we will evaluate the metal fittings using other metal materials to further improve the cost efficiency. The drawing of the metal fitting components are shown in Figures 1 and 2, with Figure 1 showing the current design which includes the polar boss, adapter and valve; and Figure 2 showing the future design which only contains the polar boss and valve and which has a much smaller polar boss opening and therefore volume.

Since the project started, we have improved the filament winding process in terms of:

1. The balance between fiber tow tension and surface curvature.
2. The balance between fiber tow tension and liner pressure.

FIGURE 1. Current Metal Fitting-Liner Interface Design

FIGURE 2. Future Metal Fitting-Liner Interface Design

3. The accuracy of fiber tow tension control.
4. The control of resin bath temperature and cure profile.

With these improvements, we increased the fiber translation efficiency (composite reinforcing efficiency) in the vessel structure from 65% to 82%. Although still lower than our target (85%), we are almost finished. With such achievement, we improved the system cost efficiency approximately from \$50.7/kWh when the project started to the current value of \$45.9/kWh, and weight efficiency approximately from 1.18 kWh/kg to 1.50 kWh/kg. If successful in achieving the target, the storage system cost efficiency will be further improved to \$45.6/kWh, and weight efficiency to 1.54 kWh/kg.

In addition to the work in the scope of this project, we propose to work on a few different tasks. Study of S-glass fiber performance in the vessel structure is one of them. The cost of S-glass fiber is about \$5.0 per pound, roughly 1/3 that of the carbon fiber we use. The replacement of carbon fiber with S-glass fiber will reduce the system cost significantly. Our study will focus on the translation efficiency we can gain from using S-glass fiber in the vessel structure, and on the safety factor we should follow on S-glass fiber. Currently the safety factor to use for S-glass fiber in the vessel structure is 3.5, determined according to the environmental and stress crack of E-glass fiber, which is much weaker and much less environmentally durable than S-glass. We believe that the safety factor for S-glass should be close to 2.25, the one people use for carbon fiber in the U.S. The estimated improvement on cost efficiency will be reported later once we have more confirmative results.

We also propose to work on components used in the storage system. Quantum has been developing more cost-efficient fuel control components. Continuous improvement will lead to a system with less components, and higher cost and weight efficiency. We have made detailed plans to reduce material usage and pursue alternative and cheaper hydrogen compatible materials, which will approximately improve the system cost efficiency from \$45.9/kWh to \$30.4/kWh. This cost cutting is contributed by the optimization of all components.

Conclusions and Future Directions

- We have very positive results in demonstrating the feasibility of a blow molding process in liner preparation, and further evaluation is on-going. Success will result in the estimated improvement of system cost efficiency from \$45.9/kWh to \$44.9/kWh.
- Material study for metal fittings is finished, and design is on-going; prototypes of new metal fitting design were made and evaluation is on-going. Success will result in the estimated improvement of system cost efficiency from \$45.9/kWh to \$44.9/kWh.
- Composite optimization through filament winding process improvement and design are 90% finished and the rest of the work is on-going. The finished work resulted in improvement of system cost efficiency from \$50.7/kWh when the project started to a current value of \$45.9/kWh.
- Propose to work on S-glass performance study in the vessel structure.
- Propose to work on component study in the storage system. Success will result in the estimated improvement of system cost efficiency from \$45.9/kWh to \$30.4/kWh.

FY 2009 Publications/Presentations

1. Low-Cost High-Efficiency High-Pressure H₂ Storage, Annual Merit Review, Department of Energy, May 18–22, 2009, Arlington, VA.
2. H₂ Tank Manufacturing Optimization, Annual Merit Review, Department of Energy, June 9–13, 2008, Arlington, VA.

IV.H.1 Purdue Hydrogen Systems Laboratory: Hydrogen Storage*

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Contract Number: DE-FC36-06GO86050

Subcontractor:
National Renewable Energy Laboratory, Golden, CO

Project Start Date: September 16, 2006
Project End Date: September 30, 2010

*Congressionally directed project

Technical Targets

On-board Storage	Units	2010/ Ultimate	Purdue 2009
System gravimetric capacity	H ₂ wt%	4.5/7.5	8.2-9.6 (material)
Overall efficiency of off-board regeneration	%	>60	Our process is being optimized

Note: the 2010/Ultimate system gravimetric densities are the revised DOE 2010 hydrogen storage targets.

Accomplishments

- Trimethyl borate was successfully converted to AB via reduction with diethylsilane in the presence of N^1,N^1,N^2,N^2 -tetramethylethane-1,2-diamine (TMEDA), followed by the displacement of TMEDA with ammonia to obtain AB.
- Increased hydrogen storage capacity of the AB slurry hydrolysis approach from 7.5 wt% to 8.2 wt% by enhancing AB/water mixing.
- Implemented continuous measurements of AB/bminCl slurry dehydrogenation and observed extremely fast hydrogen release rate.
- Investigated noncatalytic AB hydrothermolysis for a wide range of AB concentration (5-65 wt%) and temperature (75-135°C) under modest pressure (~200 psia). It was found that while varying AB concentration in the investigated range, the total hydrogen yield remains in the narrow range of 2.25-2.75 equivalent per mole of AB.
- For noncatalytic hydrothermolysis of 40 and 65 wt% AB, hydrogen storage capacity of 6.0 and 9.6 wt% were achieved at temperature ~85°C, respectively.

Objectives

- Develop an energy efficient recycling protocol for ammonia borane (AB) from spent borate.
- Develop AB slurry-based subscale onboard hydrogen storage systems.
- Develop a new noncatalytic method for hydrogen generation from AB and water.

Technical Barriers

This project addresses the following technical barriers from the Storage section (3.3.4) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan (Revision 2007):

- (A) System Weight and Volume
- (B) System Cost
- (J) Thermal Management
- (R) Regeneration Process
- (S) By-Product/Spent Material Removal

Introduction

This project allows the creation of a Hydrogen Research Laboratory in a unique partnership between Purdue University's main campus in West Lafayette and the Calumet campus. This laboratory is engaged in basic research in hydrogen production and storage and has initiated engineering systems research with goals established as per the U.S. DOE Hydrogen, Fuel Cells, and Infrastructure Technologies Program. Hydrogen production research of this project is reported in report II.J.1.

The hydrogen storage research has been focused on improving the engineering performance of AB-based onboard hydrogen storage and finding energy

efficient ways to recycle the byproducts. The AB slurry dehydrogenation work has been focused on measuring engineering properties of onboard hydrogen discharge and fresh/spent fuel transfer and developing a subscale reactor module to provide a platform for the studies of AB and other potential off-board recyclable hydrogen storage materials. Slurries provide higher energy capacity than solutions and are easier to be transported onboard than solids. In addition, we have recently proposed and demonstrated a new approach to release hydrogen from heating dilute AB solutions under modest argon pressure. During the past year, AB hydrothermolysis was studied for rich-AB/water mixtures, over a wide temperature range. The use of D_2O , instead of H_2O , was continued to clarify the reaction mechanism. Since the release of hydrogen from AB via both thermolysis and hydrolysis is exothermic, it was expected that hydrogen could be released from rich-AB/water mixtures at temperatures lower than required for pure AB thermolysis.

Approach

We are developing methods for AB dehydrogenation and regeneration that will enable its use for onboard hydrogen storage. The AB regeneration scheme is illustrated in Figure 1. The spent fuel, ammonium borate were converted to triacyl- or trialkyl borates, which provided molecules with weaker B-O bond. The reduction of triacyl- or trialkyl borates in the presence of TMEDA, followed by the displacement of TMEDA using ammonia will eventually lead to efficient ammonia borane regeneration.

We investigated ultrasonic mixing techniques to improve ruthenium (Ru) catalyzed AB slurry hydrolysis approach to obtain high hydrogen yields near stoichiometry. Also, we are designing a benchmark continuous flow AB slurry reactor module to address various common engineering issues in on-board chemical hydrogen storage systems, such as slurry handling and thermal management. To facilitate the reactor design, we are investigating AB/ionic liquid slurry dehydrogenation kinetics characterizing flowability of AB slurries and spent fuels from various

reactions including hydrolysis, thermolysis and hydrothermolysis.

The AB hydrothermolysis method for H_2 generation was studied over a wide range of AB concentrations (5-65 wt%), pressure (~200 psia) and temperature (75-135°C). To clarify the reaction mechanisms, isotopic labeling (D) was used, where measurements of H_2 and deuterium hydride (HD) concentrations in gaseous products allowed us to differentiate between the sources of the released hydrogen, i.e. AB vs. water.

Results

We computed the energetics of the steps involved in the recycling of spent borate to AB using B3LYP/aug-cc-pVDZ level of theory. We have recycled ammonia borate to AB via conversion to trimethyl borate followed by the reduction using diethylsilane. We developed novel protocol for the reduction of trimethyl borate. The reduction of trimethylborate in the presence of TMEDA using diethylsilane resulted in the formation of bisamine borane complex in quantitative yield (90%). The bisamine borane complex could be readily separated by filtration. The displacement of amine from the amine borane complex was readily achieved using ammonia in 80% yield. We have initiated energy efficient schemes to convert $NH_4B(OH)_4$ to AB via triacylborates. The advantage of conversion to such acylborate esters over simple alkylborate esters is that the B-O bond will be weakened enough to be reduced with mild hydride sources.

We studied catalytic AB water (1:2) slurry hydrolysis using ultrasonic mixing. The hydrogen yields of the four tests were 70%, 80%, 88% and 92%, respectively while the yields of tests with conventional mechanical mixing were around 75%. With 92% hydrogen yield of (1:2) AB/water slurry, the material based hydrogen storage capacity is 8.2 wt%. We also measured rheology properties of AB and sodium borohydride (SBH) spent fuels. This test, for the first time, quantitatively revealed that AB spent fuel has lower elastic stiffness (softer) and smaller viscous damping than those of SBH spent fuels. We also conducted a series of AB/ionic liquid thermolysis tests using an apparatus that allows continuous observation of hydrogen release. The AB/bmimCl mass ratio and reaction temperature were same as the tests described in the literature (Sneddon, 2008). It was observed that the reaction occurred very fast and a lot of hydrogen was released in the first minute. As illustrated in Figure 2, the hydrogen yield at 15 minutes after the beginning of reaction is same as what reported in the literature while the hydrogen release rate in the first five minutes is much faster than what indicated before (the dotted lines). This observation significantly complements the literature data and provides insightful information for system design.

FIGURE 1. AB Recycling Scheme

FIGURE 2. Continuous Measurements of Hydrogen Release of AB/bmimCl Slurry Dehydrogenation

In addition, hydrothermolysis of AB/D₂O solutions and slurries were studied in a 300-mL stainless steel Parr reactor over the temperature range 75-135°C under Ar pressure (initial) 200 psia. Mass spectral analysis of the reactor atmosphere after all experiments showed H₂ and HD as the main gaseous products. Apart from H₂ and HD, some NH₃ was also detected in the mass spectrometry analysis. It was found that for AB concentration >40 wt%, temperature (T_{reactor}) ~85°C is sufficient to release the same amount of hydrogen as at T ~135°C (Figure 3). For AB <30 wt%, however, T_{reactor} ~135°C was required instead of 85°C. As the AB concentration increased from 5 to 65 wt%, the H₂ yield increased from 0.75 to 1.75 equivalent, while HD yield decreased from 2 to 0.5 equivalent. However, the total hydrogen yield (H₂+HD) remained in the relatively narrow range of 2.25-2.75 equivalent. Thus, the role of thermolysis, as compared to hydrolysis, increases with AB concentration. As shown in Figure 2, hydrogen yield increased with AB concentration. For 40 and 65 wt% AB, hydrogen yields of 6.0 and 9.6 wt% respectively, were achieved. To our knowledge, on a material basis, the AB hydrothermolysis process is the first one to provide such high hydrogen yield values at below proton exchange membrane (PEM) fuel cell operating temperatures.

Conclusions and Future Directions

We investigated fundamental chemistry of AB recycling and achieved conversion of trimethyl borate to AB. Using ultrasonic mixing, we observed 92% hydrogen yield in catalytic AB/water (1:2) slurry hydrolysis, which provides a hydrogen storage capacity of 8.2 wt%. Also, through continuous measurements, we observed extremely fast hydrogen release rate in AB/bmimCl slurry dehydrogenation process at 120°C.

FIGURE 3. Hydrogen Yield vs. AB Concentration at P=200 psia

In addition, it was demonstrated that noncatalytic AB hydrothermolysis is a promising method for hydrogen storage. We have achieved hydrogen capacity up to 9.6 wt% using this approach, at temperature <85°C, along with rapid kinetics. To our knowledge, on a material basis, the AB hydrothermolysis process is the first one to provide such high hydrogen yield values at below PEM fuel cell operating temperatures. Further, for the same temperature range, these yield values are higher than previously reported in the literature by either AB hydrolysis or thermolysis alone.

In the near future, we will work towards maximum AB recycling yield via a novel recycling pathway. The reduction of trimethyl borate using diethylsilane will be optimized with respect to temperature and pressure, silane and amines. The displacement of TMEDA from the corresponding bisborane adduct using ammonia will be standardized for the quantitative isolation of AB. Computations of the recycling of energy efficiency will be completed. We will continue to measure engineering properties of AB aqueous and non-aqueous slurries and develop a subscale reactor module and system to address various common engineering issues in on-board chemical hydrogen storage systems. Further, the reaction mechanisms and yield of hydrogen generation from AB hydrothermolysis in aqueous solutions and slurries (>65 wt%) will be determined. The reaction by-products will also be quantified. To better understand the temperature effects (heat evolution), a smaller size reactor (~50 ml) will be developed.

FY 2009 Publications/Presentations

1. Basu, S., Brockman, A., Gagare, P., Zheng, Y., Ramachandran, P.V., Delgass, W.N., and Gore, J., 2009, "Kinetics of Ru-catalyzed Ammonia Borane Hydrolysis," *Journal of Power Sources*, 188: 238-243.

2. Diwan, M., Al-Kukhun, A., Hwang, H. and Varma, A., “Hydrogen Generation for Fuel Cell Applications,” *4th Annual Purdue Energy Center Hydrogen Initiative Symposium*, April 23, 2009, West Lafayette, IN.
3. Gagare, P., Brockman, A., Basu, S., Diwan, M., Al-Kukhun, A., Hwang, H., Zheng, Y., Ramachandran, P., Varma, A., Gore, J., “Purdue Hydrogen Systems Laboratory Part II: Hydrogen Storage,” *2009 Annual Merit Review & Peer Evaluation*, Washington, D.C.

IV.H.2 Hydrogen Storage Research*

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Project Start Date: May 19, 2004
Project End Date: August 31, 2009

*Congressionally directed project

- (C) Efficiency
- (D) Durability/Operability
- (E) Charging/Discharging Rates
- (J) Thermal Management
- (K) System Life Cycle Assessment
- (P) Lack of Understanding of Hydrogen Physisorption and Chemisorptions
- (Q) Reproducibility of Performance

Technical Targets and Critical Assumptions

This project is conducting to explore and investigate hydrogen storage materials. Insights gained from these studies will be applied toward the design and synthesis of reversible hydrogen storage materials that meet the following DOE 2010 hydrogen storage targets:

- Volumetric H₂ density, >45g H₂/L
- Gravimetric H₂ density >6.0 wt%
- Operating temperature, -30/50°C
- Delivery temperature of H₂, -40/80°C
- Cycle life, 1,000 cycles
- Fast absorption/desorption rates

Table 1 represents the critical assumptions the tasks for developing reversible hydrogen storage systems that can meet or exceed the DOE's technical targets.

TABLE 1. Progress towards Meeting Technical Targets and Critical Assumptions for Developing Reversible Hydrogen Storage Materials

Critical Assumptions	TASK 1: Li-Mg-B-N-H	TASK 2: LiMn(BH ₄) ₃ - Xmol%MgH ₂	TASK 4: PANI Nanostructures
Reversibility	Good at lower T _i specially processed materials	Reversible at moderate and high temperatures	Good at room temperature, specially processed materials
Volumetric Capacity	> 100 kg m ⁻³	> 100 kg m ⁻³	> 100 kg m ⁻³
Gravimetric Capacity	> 7.0 wt%	> 8.0 wt%	~3-10 wt% uptake
Gas Analysis	H ₂	H ₂	H ₂
Kinetics	Fast	Medium	Fast
DOE Targets Met	YES	YES	YES
Status	80% complete	70% complete	60% complete

TASK 3: Density Functional Theory Calculations to predict, validate and optimize the hydrogen storage properties of complex hydrides and nanostructures [System: Mn(BH₄)₂] – Status: 60% complete

Objectives

- Synthesis and characterization of materials with high H₂ storage potential.
- New materials and processes discovery.
- Catalytic doping, substitution and destabilization to improve the kinetics and reversibility at low temperature.
- Employ ab initio and density functional theory calculations to validate the experimental observations.
- Determine the decomposition products and pathways of materials.
- Perform analyses to assess cost effectiveness of materials including scale up.
- Reduction in the decomposition temperatures, activation energy and overall enthalpy of reaction by nanocatalyst doping, nanocrystalline admixing, etc.

Technical Barriers

This project addresses the following technical barriers from the Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) System Weight and Volume
- (B) System Cost

Accomplishments

- Successfully synthesized multinary complex hydrides involving LiNH_2 , LiBH_4 and MgH_2 using solid-state mechano-chemical process. Unique approach and adopting various processing conditions to prepare these Li-Mg-B-N-H complexes lead to efficient and reversible hydrogen storage capacity >6 wt% at 150 – 175°C . (*Acer Transactions*, 2009; *International Journal of Hydrogen Energy [IJHE]*, 2009)
- Independent validations of pressure-composition-temperature (PCT) characteristics such as H_2 storage capacity, sorption kinetics and gas evolution analysis by Southwest Research Institute® (SwRI®) of USF-processed Li-Mg-B-N-H complex hydrides. Close match of results were obtained from both SwRI® and USF experimental analysis. No evolution of ammonia and di-borane gases has been observed from the mass spectrometry studies by SwRI®. (*SwRI® Report to DOE and USF*, 2009)
- Accomplished in situ-RAMAN characteristic spectra of $\text{LiBNH}+\text{MgH}_2$ samples at the National Institute of Standards and Technology (NIST). There exists a close match between RAMAN and Fourier transform infrared analyses by both USF and NIST measurements for the identification of B-H and N-H stretches. (*NIST Report to USF*, 2009)
- Successfully synthesized complex borohydrides $\text{LiMn}(\text{BH}_4)_3$ mechanical milling of LiBH_4 and MnCl_2 . Accomplished reversibility of hydrogen sorption cycles in non-reversible hydrides $\text{LiMn}(\text{BH}_4)_3$ by self-catalyzing effects using x mol% MgH_2 . (*IJHE*, 2009)
- Nanomaterials doping and co-doping on the effective hydrogenation and dehydrogenation behavior of multinary complex hydrides (Li-Mg-B-N-H) and Li-Mn-B-H. (*USF-QuantumSphere Inc. Report* 2009)
- Established the structure of new $\text{Mn}(\text{BH}_4)_2$ phase and calculated the thermodynamic stabilities by density functional theory (DFT). (*Journal of Physical Chemistry*, 2009)
- Synthesized polyaniline nanostructures such as nanofibers and nanospheres using chemical and electrospun processes. Accomplished reversible hydrogen storage capacity of 3-10 wt% from room temperature to 100°C (*J. Nanomaterials*, 2008, *J. Nanoscience and Nanotechnology*, *J. Nano Research*, *IJHE*, 2009)

Introduction

In this study, we report the on-going hydrogen storage research on physisorption, which is the weak chemical bonding to a material, as well as

chemisorption, which is a strong chemical bond of hydrogen to a host material. Polyaniline (PANI), a conducting polymer, is investigated in both its bulk form as well as in nanostructured forms, more precisely nanofibers and nanospheres, to store hydrogen via physisorption. It is found the bulk form of polyaniline can store only approximately 0.5 wt% hydrogen, which is far short of the 6 wt% required for practical applications. Nanofibers and nanospheres, however, have been developed, which can store between 4 wt% and 10 wt% of hydrogen at room temperature with varying kinetics. A new complex metal hydride comprised of LiBH_4 , LiNH_2 and MgH_2 has been developed to store hydrogen via chemisorption. While the parent compounds require high temperatures and suffer of slow kinetics for hydrogen sorption, the work performed as part of this time period shows that optimized processing conditions reduce the hydrogen release temperature from 250°C to approximately 150°C , while the addition of nano-sized materials has been found to increase the kinetics of hydrogen sorption as well as further decrease the hydrogen release temperature, making this one of the first viable hydrogen storage materials available. We have also successfully studied the hydrogen storage performances in novel complex borohydrides and their destabilized counterparts, $\text{Mn}(\text{BH}_4)_2$, $\text{LiMn}(\text{BH}_4)_3$, and $\text{LiMn}(\text{BH}_4)_{3-x}$ mol% MgH_2 by both theoretical and experimental approaches. It is noteworthy to mention that for the first time that nanostructured polyaniline has been investigated for its reversible hydrogen behavior. Additionally, the thorough investigation of the effects of nano sized additives and processing parameter optimization of the multinary hydride and advanced complex borohydrides are first reported.

Approach

Selection and synthesis of complex hydrides; structural/microstructural/chemical characterization; volumetric, gravimetric and thermal analysis; activation energy by Kissinger's method; gas quantification analysis using gas chromatography (GC) and mass spectrometry (MS); and DFT to study the crystal structure and thermodynamic stability of complex borohydrides and multinary complexes.

Results

Task 1. Destabilized Multinary Complex Hydrides ($\text{LiBH}_4/\text{LiNH}_2/\text{MgH}_2$)

The present work addresses the grand challenge of hydrogen storage by mechano-chemically milling LiBH_4 and LiNH_2 with MgH_2 to produce a new complex quaternary Li-Mg-B-N-H structure. This Li-Mg-B-N-H structure possesses storage capacity of more than 10 wt% at around 150°C . The parent compounds, LiBH_4

and LiNH_2 , were purchased from Sigma Aldrich with a purity of at least 95%, while MgH_2 was obtained from Alfa Aesar with a purity of 98%. All materials were kept in an inert atmosphere in a glove box and used without further purification. The investigated samples were created in 4 g batches with a constant molar ratio of $2\text{LiNH}_2:\text{LiBH}_4:\text{MgH}_2$, while taking into account the purity of the parent compounds, by employing high energy ball milling (Fritsch Pulverisette 6) for 5 hours at 300 rpm with intermittent hydrogen/argon (5%/95%) purges for 20 minutes before milling and after 2 and 4 hours. This was done to ensure that as little hydrogen as possible was released during the milling process and to reduce the agglomeration of the hydride that occurs when pure hydrogen is used as compared to the hydrogen/argon mixture. The MgH_2 was either added as received or was added as a so-called nano MgH_2 . The nano MgH_2 (nMgH_2) was created by ball milling the commercial MgH_2 (cMgH_2) for 12 hours with intermittent hydrogen/argon purges every 2 hours. This ensured the reduction of particle size as well as the decrease in hydrogen release temperature, as previously reported. Figure 1(a) shows the X-ray diffraction (XRD) pattern comparing the five differently processed complex hydrides. The addition of commercial MgH_2 does not cause the formation of a new complex structure, but instead indicates that the quaternary structure (LiBNH) is preserved, while the MgH_2 simply intermixes with the material.

Upon producing the complex hydrides, each sample was characterized for its thermal desorption characteristics using temperature-programmed desorption (TPD) with a heating rate of 1, 5, 10, and $15^\circ\text{C}/\text{min}$. As compared to the quaternary structure, the multinary structure containing MgH_2 showed a 3-step hydrogen release mechanism. Figure 2 represents the PCT isotherms of the multinary complex hydrides created with different processing conditions. The PCT characteristics of USF's complex hydride Li-nMg-B-N-H were also performed at SwRI[®]. Interestingly, these complex hydrides exhibited reversible hydrogen storage behavior and are shown in Figure 2(a). A reversible hydrogen storage capacity of 5-7 wt% was reproducibly obtained for these materials. The cyclic kinetics of Li-nMg-B-N-H reveals a reversible hydrogen storage capacity of 6-8 wt% with fast sorption kinetics around $200\text{--}250^\circ\text{C}$ which matches or exceeds with the set-forth DOE technical targets. With respect to the MS analyses, SwRI[®] reported that the scans did not reveal any evidence for potential parent (or daughter) species (ions); namely, NH_3 , BH_3 , BH_2NH_2 , N_2H_4 .

Task 2. Destabilization of Transition Metal Complex Borohydrides [$\text{LiMn}(\text{BH}_4)_3 + \text{Xmol}\%\text{MgH}_2$]

Synthesis of the new complex hydride, $\text{LiMn}(\text{BH}_4)_3$ from the parent compounds LiBH_4 and MnCl_2 (3:1)

FIGURE 1. (a) XRD (b) TPD Profile of the five differently processed materials as well as the parent compounds, LiBH_4 , LiNH_2 , MgH_2 and nano MgH_2 .

was carried out in solid state employing the mechano-chemical milling process. The reactions proceed based on the stoichiometric ratio given in the equation (1) below,

We have demonstrated the successful preparation of new alkali-transition metal-based complex borohydrides, $\text{LiMn}(\text{BH}_4)_3$ from the precursors of LiBH_4 and MnCl_2 by the mechano-chemical process. To reduce the decomposition temperature further, we have attempted to dope the $\text{LiMn}(\text{BH}_4)_3$ with different mole concentrations of nanomaterials (nano-Ni). It was clearly noticed that doping with nanoNi lowers the decomposition temperature and at the same time enhances the kinetics of the reaction. It is unambiguously seen from the thermogravimetric analysis and TPD analyses that nano-Ni doping of

FIGURE 2. (a) PCT and (b) Hydrogen Cycling Kinetics of Li-Mg-B-N-H Complex Hydrides at Different Temperatures

1-2 mol% destabilizes the structure with at least 10-20°C reduction in hydrogen thermal decomposition temperature (T_{dec}). Moreover, the nano-Ni has greater effect on the hydrogen release (desorption kinetics) rate when compared to the undoped $\text{LiMn}(\text{BH}_4)_3$ as observed in Figure 3(a). The optimum concentration of nano-Ni was found to be 1-2 mol% which can speed up the initial decomposition reaction at least 2 to 3 times when compared to the undoped counterpart. In order to further confirm the reversible hydrogen storage behavior of this MgH_2 admixed LiMnBH , we have systematically executed PCT measurements at constant temperatures of 100°C. Figure 3(b) demonstrates the reversible hydrogen sorption behavior at 100°C with total capacity of 3.5 wt%.

Task 3. Polyaniline (PANI) Nanofibers (Chemical and Electrospun Methods)

Conducting polyaniline nanofibers were synthesized using chemical templating method followed by

FIGURE 3. (a) Dehydrogenation Kinetics and (b) PCT of $\text{LiMn}(\text{BH}_4)_3$ and $\text{LiMnBH-Xmol}\%\text{MgH}_2$

electrospun process. Figure 4(a) shows the cycle life kinetics of the electrospun PANI nanofibers. No hydrogen uptake was observed until the sample was heated to 100°C. The initial high capacity of 11 wt% is not fully observed when desorbing the hydrogen, as only 8 wt% is released. This occurs in a two-step process characterized by a fast (physisorption) hydrogen release and a slower (chemisorption) hydrogen release step. This hydrogen behavior is due to hydrogen bonding with both unterminated bonds as well as with the surface of the nanofibers. The PANI nanofiber chemical method, however, absorbed hydrogen at 30°C and did so reversibly with a capacity of approximately 3wt%, as seen in Figure 4. Unlike the electrospun nanofibers, the hydrogen was absorbed and released in a one-step process with very rapid kinetics of less than 10 min. This fast hydrogen sorption is most likely due to the higher surface area of the chemically grown nanofibers as opposed to the electrospun nanofibers that exhibit a much smoother surface. The surface morphologies before and after hydrogen sorption of these PANI nanofibers encompass significant changes in the microstructure (nanofibrillar swelling effect) which clearly suggest effective hydrogen uptake and release.

FIGURE 4. Hydrogen Cycling Kinetics in Polyaniline Nanofibers Prepared by (a) Electrospun (b) Chemical Methods

Conclusions

- Complex borohydrides $\text{LiMn}(\text{BH}_4)_3$ has been successfully synthesized from the solid state mechano-chemical process of $\text{Na}(\text{Li})\text{BH}_4$ and MnCl_2 .
- The thermal decomposition of $\text{LiMn}(\text{BH}_4)_3$ exhibits weight loss due to hydrogen desorption of around 9.0 wt% at $\sim 150^\circ\text{C}$ (same or exceeds the DOE and FreedomCAR targets).
- Destabilization of the complex hydride mixture $\text{LiBH}_4/\text{LiNH}_2/\text{MgH}_2$ produces multinary hydride structure for reversible hydrogen storage behavior at moderate temperatures.
- Among the various methodologies, nano- MgH_2 mixed with quaternary LiBNH structure showed relatively enhanced hydrogen decomposition characteristics as observed from TPD.
- PANI nanofibers and nanospheres have been prepared from chemical and electrospun synthesis route. Hydrogen cycling kinetics measurements demonstrate promising reversibility.

Future Directions

- NanoPd and NanoAg doping on the hydrogen decomposition characteristics of $\text{LiMn}(\text{BH}_4)_3$.
- Analysis of the residual gas after thermal decomposition of $\text{LiMn}(\text{BH}_4)_3$ by GC/MS.
- Hydrogen sorption measurements (full cycle life kinetics, PCT, etc.) of nanocatalysts doped with LiAlH_4 +nano MgH_2 complex mixture.
- Estimation of enthalpy of reaction from the van't Hoff equation from the PCT data.
- GC/MS of the desorbed gases during dehydrogenation process.
- Thermodynamic characterization of the USF developed Li-Mg-B-N-H complex materials.
- New discovery of materials with nanocatalyst doping.
- Reproducibility and repeatability of optimized materials for the high reversible hydrogen sorption behavior.
- Activation energy calculations with different processing conditions to estimate and understand the effects of nanocatalyst dopants.
- Synthesis of polyaniline nanofibers by chemical and electrospun method to increase the surface area and hydrogen reaction sites.

Special Recognitions & Awards/Patents Issued

- S.S. Srinivasan, M.U. Jurczyk, E.K. Stefanakos and D.Y. Goswami, Methods and processes for producing complex hydrides exhibiting high hydrogen storage capacity and fast sorption kinetics at moderate temperatures, *Non Provisional patent (Electronic file application number: 61037869)*, University of South Florida, Tampa, FL, USA, 2007.
- Won a *Grant Proposal competition* from the California-based Nanomaterials Manufacturing Company QuantumSphere Inc., 2008-2009.

FY 2009 Publications/Presentations

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- M.U. Niemann, S.S. Srinivasan, A.R. Phani, A. Kumar, D.Y. Goswami, E.K. Stefanakos, Electrospun polyaniline nanofibers for hydrogen storage, *J. Nano Research*, 2009, In Press.
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IV.H.3 NaSi and Na-SG Powder Hydrogen Fuel Cells*

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Contract Number: DE-FG36-08G088108

Subcontractors:

- Trulite Inc., El Dorado Hills, CA
- University of Texas, CEM, Austin, TX

Project Start Date: August 1, 2008
Project End Date: January 31, 2010

*Congressionally directed project

Objectives

- Develop and demonstrate a controllable hydrogen generation system based on sodium silicide powder for portable fuel cell applications.
- Develop specific reaction control mechanisms which encompass water feeding, thermal management, and reaction site maximization.
- Verify operation of all core balance of plant and reaction control components in a laboratory setup.
- Design, fabricate, and assemble a prototype system packaged in a professional manner which generates controlled hydrogen with minimal user intervention.
- Demonstrate operation with a fuel cell system capable of 250 W.
- Conduct core research to evaluate the potential for ultra-high performance sodium silicide materials.
- Develop the appropriate manufacturing methods to readily scale production of sodium silicide in follow-on activities.

Technical Barriers

This project addresses the following technical barriers of the Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) System Weight and Volume
- (B) System Cost
- (J) Thermal Management

Technical Targets

The developed sodium silicide technology is specifically focused on portable power applications such as back-up power, mobile workstations, and emergency responders. The target range includes applications from 50 to 500 W. The developed technology is expected to be scalable to at least 1 kW for applications such as lawn mowers that are known to be highly polluting.

The developed technology will likely not meet all DOE technical targets for automotive applications, but there is a significant focus on customer attributes such as fast starting, rapid restarting, low pressure, and ease of use. The specific technical targets are discussed below.

The primary focus of the current effort is to establish system technology using sodium silicide. SiGNa anticipates the development of advanced silicides with comparable system control architectures which will further increase performance metrics. The specific energy can reach up to 1,734 W-hr/kg (lower heating value) including all reaction water, power and packaging for the current commercial sodium silicide material. Further research is required to understand and optimize the over-stoichiometric water required in the silicide reaction. Advanced silicides, which are currently under development, will yield a specific energy of up to 2,125 W-hr/kg.

The cost will approach DOE targets even for small portable applications. The cost is expected to reach \$4.47/kW-hr. Further cost reductions are possible which may be enabled by manufacturing scale up and the industrial usage demands of sodium silicate.

Accomplishments

Significant progress has been made in the development of a standalone hydrogen generation system for fuel cell applications. These accomplishments are summarized by the following:

- Completed laboratory system and demonstrated key performance attributes: >9 wt% hydrogen yield on a

powder basis, multiple re-starts with up to 1 week of off-time, and controlled generation (~3 slpm) at low pressures (~30 psi).

- Have successfully completed bench top testing and sustained operation of a 300 W fuel cell-powered electric bicycle.
- Developed a hydrogen purity filtration system and verified results with gas chromatography verifying 99.99% hydrogen purity.
- Completed design of stand alone hydrogen generation development unit.

Introduction

SiGNa Chemistry, Inc. is developing a unique hydrogen storage mechanism utilizing SiGNa's air-stable sodium silicide powder derivatives (e.g. NaSi). SiGNa's stabilized powders have been shown to produce up to 9.8 wt% H₂. The primary goal is to develop a prototype system including all balance-of-plant components which generates hydrogen in a controlled manner based on usage requirements. SiGNa Chemistry will initially target a hydrogen generation system yielding approximately 3 slpm. This level of hydrogen generation can support a wide range of applications such as: supplemental hydrogen for diesel trucks for improved fuel efficiency and reduced emissions, primary power for small vehicles (i.e. scooters, mini-bikes), emergency responder stations, backup power, surveillance, and other off-grid applications. For reference, 3 slpm of H₂ will net approximately 250 W in fuel cell applications.

While numerous chemistries have been explored for hydrogen production for portable systems such as sodium borohydride or methanol reforming, hydrogen storage commercialization has been limited to high pressure tanks and metal hydrides both of which have significant usability issues. SiGNa's newly developed class of sodium silicides such as, NaSi, rapidly react with water to form hydrogen and a benign waste product, sodium silicate.

SiGNa has developed systems implementation technology to facilitate this reaction in a manner that is highly controllable with high flow capability at low pressures with excellent re-start characteristics.

Approach

The overall approach is summarized in Figure 1. The basic architecture is straightforward; simply add water to powder. Water solutions, such as salt water, may also be employed for lower temperature operation

or other reaction tuning parameters. In practice, a micro-spray water distribution system has been developed to increase the active reaction area. For a "single-start" reaction, this distribution system is not necessary as the bed will self-churn and fully react large quantities of powder. To rapidly start a cold, partially reacted solution, the micro-spray system serves to spray water streams on un-reacted powder throughout the chamber.

SiGNa first developed a series of clear reaction vessels to visualize the reaction and optimize the parameters. This series of breadboard test vehicles is used to test the various control components and demonstrate the core reaction characteristics. The results of these experiments are being incorporated to develop a standalone hydrogen generation system. This system will be tested in conjunction with a fuel cell/battery hybrid system against a range of operational scenarios.

The materials to date have only been manufactured on a lab scale. SiGNa is currently working with an established toll manufacturer with expertise in alkali metals to develop the next generation manufacturing process.

Results

Three different breadboard reactors have been fabricated and tested in a range of ~60 to ~1,200 ml. The primary areas of development and testing have been: water feeding and distribution, hydrogen separation, control system and balance-of-plant components, and the hydrogen purity system.

The water feed and distribution system primarily consists of the pump and micro-nozzle network. In practice, there are significant challenges in getting a far reaching spray at very low water flows (< 1 ml/min). The water distribution network is almost exclusively required for re-start conditions. The laboratory systems have shown the ability to rapidly restart after storage at room temperature for 7 days (Figure 2). In this test, the reactor was tested for a total of five starts with each run generating about 1/5 of the total available hydrogen. It is also required near the end of the reaction to ensure maximum powder reactivity. The water feed system was also modified to incorporate the spray nozzles directly over the separation membrane to minimize filter clogging.

A significant amount of work was done early in the project with the small reactors in the selection of separation membranes. For the small reaction chambers, significant foaming could readily cause filtration clogging. A filter spray system was developed to breakdown the foaming. This enabled significant improvements in the separation membrane pressure drop (Figure 3). The developed separation membrane

FIGURE 1. Development Approach Including Laboratory Test Systems and Controlled Hydrogen Generation

FIGURE 2. Restart Example After 7 Days at Room Temperature

FIGURE 3. Impact of Filter Spray and Separation Membrane Resistance

included a sandwich of multiple layers. The much larger reactors have had very little foaming issues as the surface tension forces are typically insufficient to develop foam over the larger reactor area. However, the developed components are still utilized on the larger canisters for robustness and to ensure operation in non-typical operating scenarios such as vibration, upside down storage, etc.

The balance-of-plant components including check valves, on/off valves, sensors, and pumps have been selected and tested. In addition, a custom controller was developed with prediction control loops to handle the various start/stop and operational scenarios. While the basic start/stop and operational testing has been completed, additional work is required in this area.

SiGNa has also completed the design of the majority of the stand alone system components (Figure 4). SiGNa anticipates design completion and fabrication over the coming weeks.

Conclusions and Future Directions

Sodium silicide has been shown to be capable of controlled hydrogen flow for a range of portable applications. A number of system implementation issues that have plagued other hydrolysis systems impacting restart capability have been resolved. All results continue to indicate that sodium silicide is capable of near term commercialization while providing a hydrogen source that is safe and easy to use. The balance of work in this project will be focused in the following areas:

- Design completion of the stand along hydrogen generation system.
- Completion of the fabrication, assembly, and testing of the standalone hydrogen generation system
- Continued testing on larger powder size runs to optimize control characteristics and minimize water usage. The largest run to date was ~150 grams of powder yielding ~15 grams of hydrogen. SiGNa anticipates the demonstration of at least 30 grams of hydrogen in a thin walled, low pressure hydrogen generation canister.

FIGURE 4. Stand-alone Hydrogen Generation and Fuel Cell Test System With Water Recirculation Capability Under Development

- Continued testing and verification of hydrogen purity over a range of particle size and operational scenarios.
- Demonstrated operability and usability in conjunction with a >250 W fuel cell.

Special Recognitions & Awards/Patents Issued

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FY 2009 Publications/Presentations

1. DOE Annual Review, May 2009.

IV.H.4 An Integrated Approach for Hydrogen Production and Storage in Complex Hydrides of Transitional Elements and Carbon-based Nanostructural Materials*

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Project Period: July 1, 2006
Projected End Date: July 31, 2010

*Congressionally directed project

Objectives

The goal is to produce hydrogen economically using photo-electrochemical (PEC) electrolysis of water directly from sunlight with corrosion resistant semiconductor electrodes for catalytic conversion. The specific objectives are:

- Improve (a) photo-conversion efficiency (solar-to-hydrogen ratio) to 10 percent evolving H_2 and O_2 and (b) photo-corrosion resistance of photo-anodes for 5,000 hours of operation generating H_2 from water.
- Synthesize photoanodes maximizing both light absorption and photoactive sites for high solar-to-hydrogen conversion.
- Develop a hybrid semiconducting photoanode, $TiSi_2$, with a corrosion inhibiting TiO_2 protective layer.
- Use heterogeneous, nanostructured, and hybrid semiconductor photoanodes consisting of layered electrodes made of $TiSi_2$ and TiO_2 for electrolyzing water, and perform fundamental studies on surface energetics: (a) control of surface states, (b) minimization of traps that are responsible for recombination of photo-excited charge carriers at

the interface, and (c) reduction of photocorrosion of semiconductor electrodes.

- Increase of reversible hydrogen storage capacity in complex metal hydrides by developing new systems including hydride phases,
- Investigate the effects of nanostructures on adsorption/desorption kinetics, and study surface oxidation properties.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

Hydrogen Production (3.1.4.2.6)

- (AP) Materials Efficiency
- (AQ) Materials Durability
- (AS) Device Configuration

Hydrogen Storage (3.3.4.2)

- (P) Lack of Understanding of Hydrogen Physisorption and Chemisorption

Technical Targets

Hydrogen Production

Our technical target is to reach the DOE goals:

- Chemical conversion process efficiency: 10% by 2010 and 12% by 2015
- Plant solar-to-hydrogen efficiency: 8% by 2010 and 10% by 2015
- Hydrogen production cost: \$3.00/gge (approximately 1 kg of H_2) by 2018

Hydrogen Storage

This project is also conducting studies of complex hydrides (borohydrides and alanates $LiBH_4$, $Ca(BH_4)_2$, $NaAlH_4$) that are considered to have potential for reversibly storing large amounts of hydrogen. Effect of nanostructured materials using glancing angle deposition (GLAD) on kinetics and oxidation is being studied. Insights gained from these studies will be applied toward the design and synthesis of hydrogen storage materials.

This portion of the project will work towards achieving, among others, the following key DOE 2010 hydrogen storage system targets:

- System gravimetric energy capacity: 2 kWh/kg
- System volumetric energy capacity: 1.5 kWh/L
- System cost: \$4/kWh

Accomplishments

Hydrogen Production

- Titanium disilicide (TiSi_2) thin films as a part of composite multilayer high efficiency photoanodes for hydrogen generation have been synthesized.
- Electrochemical synthesis of patterned TiO_2 nanorods and nanotubes with separations comparable to wavelength of visible light for trapping solar radiation.
- Multi-layered photoanodes for high efficiency photo-conversion and minimization of photocorrosion.
- Plasma treatments of photoanodes for (a) removing charge traps, (b) surface doping with nitrogen, (c) creating oxygen vacancies for achieving high photocurrent density.
- Design of prototype PEC hydrogen generator with a solar radiation concentrator for optimized operation.

Hydrogen Storage

Decomposition studies have been performed on LiBH_4 , $\text{Ca}(\text{BH}_4)_2$ and NaAlH_4 primarily aimed at species and chemical mechanism identification. A study of the catalytic interactions of transition metal alloys in borohydride thermolysis has been initiated. The potential for novel synthesis methods has been demonstrated for $\text{Ca}(\text{BH}_4)_2$.

The GLAD technique was utilized for the growth of nanostructured arrays in the shapes of vertical nanoblades and nanorods. Mg nanostructures as a model material system have been studied. Hydrogen storage capacity, adsorption/desorption kinetics, thermal stability, and oxidation properties of Mg nanostructures and conventional thin films have been investigated. Significant increase in low temperature hydrogen storage values (e.g. ~4.8 wt% @ 100°C) has been observed for Mg nanostructures compared to Mg thin films (e.g. ~0.8 wt% @ 100°C). A new quartz crystal microbalance (QCM) system was developed and upgraded for the kinetic investigation of hydrogen storage capacity and adsorption/desorption kinetics properties of nanostructured and thin film coatings. In addition, we have started investigating magnesium borohydride and

alanate for GLAD nanofabrication and hydrogen storage studies.

Approach

The experimental studies was organized into two major tasks with several subtasks: (1) Hydrogen Production: Task 1.1, Photo-Electrolysis of Water; Task 1.2, UV/Solar Splitting of Water Using Nanostructured Materials; (2) Hydrogen Storage: Task 2.1, Metal Hydride/Storage Materials Screening; Task 2.2, Plasma Reactor Enhanced Hydrogen Storage; Task 2.3, Characterization of Hydrogen Storage Materials.

Hydrogen Production

Our approach has been focused on the design and construction of an integrated laboratory-scale self-standing PEC-based hydrogen generator using heterogeneous, nanostructured hybrid layered electrodes made of TiSi_2 and TiO_2 semiconductors.

Hydrogen Storage

Our approach will focus on a study of a series of functionally similar hydrides. Hydride complexes that have been more widely characterized by other groups will be tested for verification of our experimental procedures, validation of reproducibility of the hydride and as reference data for model development. Meanwhile, related hydride complexes that are less well documented, or have yet to be investigated for use as storage medium will be investigated for feasibility.

For the fabrication of magnesium nanostructures, we will use a novel oblique angle deposition set-up (i.e. GLAD) in the laboratory of Dr. Karabacak. This set-up allows the deposition through direct current/radio frequency sputtering or thermal evaporation of materials on 2" size substrates attached on a special holder which can be tilted to a given angle and can be rotated at a given speed. A homemade QCM system will be used for the investigation of hydrogen storage, thermal stability, and oxidation properties of nanostructures and thin films produced.

Results

Hydrogen Production

- Development of titanium disilicide thin films as a part of composite multilayer high efficiency photoanodes for hydrogen generation (Figures 1, 2).
- Deposition of thin layer of TiSi_2 (Figure 1).

FIGURE 1. Scanning Electron Microscope Image of a Titanium Silicide Film on a Silicon Substrate

FIGURE 2. Application of layered photoanodes using TiSi_2 and TiO_2 semiconductors. Titanium disilicide (TiSi_2) electrode with coating of a transparent TiO_2 electrode to be used for studying the PEC activities.

- Development of patterned nanotubular structure by ramping voltage during electrochemical anodization process (Figure 3).

FIGURE 3. Current transient during anodization of Ti while ramping the voltage from 60 V to 20 V.

FIGURE 4. Design of two-layered nanotubes in packed form with their outer walls in contact with each other (left) and two-layered nanotubes with their walls separated from each other with spacing equal to the wavelength of incident light (right). The separation between the walls traps incident light for improved absorption.

- Design of two-layer nanotubes of TiO_2 and TiSi_2 (Figure 3).
- Nanotube fabrication with stepped voltage anodization (Figure 4).
- Optimization of nitrogen plasma treatment process for maximizing photocurrent density.

Hydrogen Storage

While our studies of the thermal decomposition of NaAlH_4 agree well with published literature, proceeding at a repeatable rate through the clearly identifiable intermediate compound Na_3AlH_6 , the decomposition of borohydride compounds have proven more difficult to analyze. The decomposition of LiBH_4 , for instance, has yielded yet unidentified products on numerous occasions (Figure 5). We have observed that the decomposition reaction can be ‘catalyzed’ by huge range of compounds including transition metals (e.g. nickel), alloys (LaNi_5), non-metals (SiO_2 [1] and carbon nanotubes [2]) with similar effect. The reason for this and the mechanism is yet unknown.

As regards our nanostructured approach (Figure 6), significant increase in low temperature hydrogen storage values (e.g. $\sim 4.8 \text{ wt\%}$ @ 100°C) has been observed for Mg nanostructures compared to Mg thin films (e.g. $\sim 0.8 \text{ wt\%}$ @ 100°C).

FIGURE 5. Pressure vs. time and temperature vs. time curves for decomposition of LiBH_4 in helium atmosphere under a pressure of 15 psi. The top curves in both figures correspond to 400 mg of pure LiBH_4 , whereas the middle and bottom curves correspond to additives – LaNi_5 and elemental Ni – of mass 40 mg each. The behavior is very similar to Fang et al. [2].

FIGURE 6. Hydrogen storage in Mg thin film and GLAD nanoblades at different temperature intervals.

Conclusions and Future Directions

Hydrogen Production

The present work reports the importance of systematic investigations of (1) the geometric structure of the nanotube arrays, (2) the plasma process for surface doping of TiO_2 nanotubular photoanode with N for decreasing surface bandgaps and (3) annealing

process for crystallization for improving photocatalytic generation of hydrogen by splitting water. The test results show promising aspects of tuning several parameters involved in photoelectrochemical processes in improving conversion efficiency.

Hydrogen Storage

It is unlikely that borohydrides will be a viable reversible storage medium until the decomposition/dehydrogenation reaction is better understood. More knowledge of the chemical mechanisms involved must be obtained to allow for better control of the reaction, products, reversibility and catalysis. Future studies will be aimed at elucidating the chemical mechanism of decomposition and catalytic mechanisms contributed by additives.

We will study the effect of catalysis addition, nanostructure size, shape and separation on hydrogen storage properties of nanostructured Mg as a model system. In addition, we plan to investigate hydrogen storage properties of thin films and nanostructures of magnesium alanate and borohydride.

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IV.H.5 Hydrogen Fuel Cells and Storage Technology Project*

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Contract Number: DE-FG36-05GO85028

Subcontractor:

UNLV, Las Vegas, NV

Collaborating Partner:

UTC Power, Inc, South Windsor, CT

Project Start Date: September 15, 2005

Project End Date: December 31, 2009

*Congressionally directed project

Objectives

- Study the electronic structure of nanomaterials for hydrogen storage to develop detailed understanding of hydrogen adsorption/absorption and desorption mechanisms.
- Investigate electronic structure, bonding and catalytic activities of pure and alloyed transition metal clusters for fuel cell applications.
- Collaborate with UTC in the development of efficient catalysts for fuel cell applications
- Develop new cost-effective hydrocarbon-based polymer electrolyte membranes with improved performance relative to Nafion[®], especially at high temperature (120°C) and low humidity.

Technical Barriers

This project addresses the following technical barriers from the Storage and Fuel Cells sections of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

Storage barriers addressed by this project:

- (A) System Weight and Volume
- (D) Durability/Operability
- (P) Understanding of Hydrogen Physisorption and Chemisorption
- (Q) Reproducibility of Performance

Fuel Cells barriers addressed by this project:

- (A) Durability
- (B) Cost
- (C) Electrode Performance

Technical Targets

This project applies closely-coupled theoretical and experimental studies to gain fundamental understanding of hydrogen interaction with different nanostructured materials, fuel cell catalysis, and development of new fuel cell membrane materials. Topics of ongoing studies include:

- Hydrogen adsorption/desorption in various pure and doped matrices.
- The electronic structure of carbon nanostructures with metal adatoms including effects of adsorbed hydrogen molecules and atoms.
- Catalytic surface degradation mechanisms for fuel cell catalysts.
- Synthesis and performance of mesoporous polymer/metal nanostructures for hydrogen storage.
- Development of new sulfonated fuel cell membranes that meet DOE 2010 technical targets and that can outperform state-of-the-art Nafion[®] membranes at high temperature (120°C) and low relative humidity.
- Electronic structure, bonding, and dynamics and kinetics of adsorption/desorption processes.
- Hydrogen interaction, dissociation, and saturation on pure and alloyed transition metal clusters.

Accomplishments

- A detailed study of the adsorption of Ti and Li on carbon nanomaterials revealed oxidation

challenges of Ti adatoms that can be overcome by Li coadsorption.

- Studies of fuel cell catalysts prepared at UTC established their oxidation behavior as a function of annealing temperature and acid leach conditions.
- Synthesis and characterization of polyaniline/Pd composites established their potential for hydrogen storage.
- Fluorine substituted sulfonated proton exchange membranes (PEMs) performed better than Nafion® in proton conductivity and demonstrated acceptable water uptake.
- Quantified electronic structure, bonding, and hydrogen interaction and saturation of pure and alloyed clusters of Ti, Sc, and Zr.
- Investigated the role of external electric fields on hydrogen adsorption on transition metal clusters.

Introduction

Design and development of improved low-cost catalytic materials and high-capacity hydrogen storage media are paramount to enabling the hydrogen economy. Presently available catalysts are mostly precious metals in pure or alloyed form and their high cost limits wider use in fuel cell applications. Similarly, materials with optimum hydrogen storage properties are yet to be designed. Both these properties are intimately linked to the electronic structure, morphology, size, etc. of the chosen materials. Here, we present results of combined theoretical and experimental studies of electronic structure, bonding, and hydrogen adsorption/desorption characteristics of a number of different nanomaterials and metal clusters. We further explore issues associated with oxidation of Ti-doped carbon-based materials and how oxidation can be minimized by doping with lithium. We also discuss the hydrogen storage properties of polyaniline/Pd composites synthesized at UNLV.

Most ionomer materials currently being tested in PEM fuel cells demonstration units are based on perfluorosulfonic acid (PFSA) polymers such as Nafion®. However, shortcomings of these materials seriously limit wide application of fuel cells as power sources. We discuss properties of new hydrocarbon-based high-performance sulfonated PEMs that can be manufactured at low cost.

Approach

We have performed deposition of metals (Ti and Li) on carbon nanomaterials (single-wall carbon nanotubes [SWCNTs] and C₆₀) under ultra-high vacuum (UHV) conditions and investigated the chemical and electronic structures using laterally integrating spectroscopic

techniques. The objectives are to understand the impact of the metal deposits on the surface of carbon nanostructures, the oxidation behavior of the metals, and the consequences for their application in hydrogen storage.

We have continued our studies of Pt-based fuel cell catalysts prepared at UTC and UNLV. The samples were measured using synchrotron- and lab-based soft X-ray and ultraviolet spectroscopies in order to understand their chemical properties, to investigate the presence (or absence) of a core-shell structure, and to gain insight into their electronic properties.

Pd/polyaniline composites were prepared using two different methods of Pd incorporation, namely chemical synthesis using either Pd(IV) or Pd(II) and the monomer/oligomer, as well as electrochemical synthesis of polyaniline followed by reduction of Pd(IV) or Pd(II).

Aromatic polyamides are known to have excellent chemical stability and mechanical properties that are critical features for an effective PEM in fuel cell applications. Initial results of sulfonated aromatic poly(ether amide) showed proton conductivity that is comparable to that of Nafion® at 80°C and 100% relative humidity. To improve proton conductivity of the membrane further while preventing excessive water uptake, synthesis efforts to incorporate fluorinated moiety along the polymer chains have been undertaken.

Results

X-ray photoelectron spectroscopy (XPS), ultraviolet photoelectron spectroscopy, and work function spectra of SWCNTs before and after Ti deposition show evidence of Ti-C bond formation. A similar interaction between Ti adatoms and C₆₀ was observed and attributed to the hybridization of Ti 3d orbitals with the highest occupied molecular orbital and lowest unoccupied molecular orbital levels of the C₆₀ molecules. The deposited metallic Ti adatoms also strongly adsorb oxygen-containing species and become oxidized, even under UHV conditions. Figure 1a shows the increase of the O 1s XPS signal after the Ti-deposited SWCNT sample was stored in UHV (~10⁻¹⁰ mbar) for 2, 18, and 40 hours. Consequently, the metallic Ti adatoms were oxidized, as shown in Figure 1b, with the formation of Ti oxides. The oxidation of Ti is a great concern, because it would affect the suitability of the Ti-deposited systems as hydrogen storage materials. Primary results of a co-evaporation of Li and Ti on Au substrates have demonstrated that Li can be used to reduce Ti oxides after exposing the Ti-deposited sample to air. Thus, a co-evaporation experiment of Li and Ti was performed on a SWCNT sample to test whether a similar effect can be observed for SWCNT substrates. Indeed, preliminary XPS experiments confirm the reduction of the TiO₂ component and the re-appearance of the intermediate

FIGURE 1. a) Increase of O1s XPS signal as a function of storage time in UHV (10^{-10} mbar) due to adsorption of oxygen species on the Ti-deposited SWCNTs; b) Oxidation of deposited Ti adatoms and formation of Ti oxides

Ti oxides and metallic Ti components after subsequent deposition of Li on the oxidized Ti/SWNT sample.

A new set of Pt-based bimetallic nanoparticle catalysts with carbon black support (PtIr/KB) prepared at UTC Power was studied using lab-based soft X-ray spectroscopies. The two measured samples were annealed at 700 and 1,000°C, respectively. Based on O 1s XPS spectra, the oxygen atoms in the samples exist in at least two different chemical environments, metal oxides and hydroxides. The overall O 1s peak area decreases with increasing annealing temperature, indicating that higher annealing temperatures are more effective in reducing the oxygen concentration on the nanoparticle catalysts. However, the presence of the metal oxides even after annealing suggest that

FIGURE 2. O 1s and Pt $4p_{3/2}$ XPS spectra of Pt_3Co/KB samples prepared at UTC and UNLV under different annealing temperatures and environments as listed (unless otherwise noted, samples were annealed under Ar flow). Spectra were normalized by the count rate at the low-binding energy side of the Pt $4p_{3/2}$ peak.

the current annealing process is not sufficient to fully remove the oxygen content from the samples. To address the impact of sample preparation process on the electronic structures of Pt-based bimetallic nanoparticle catalysts, we annealed Pt_3Co/KB samples at UNLV under either UHV environment or Ar gas flow, and compared to the samples shipped from UTC, which were annealed under Ar gas flow. Figure 2 shows O 1s and Pt $4p_{3/2}$ XPS spectra of the Pt_3Co/KB samples, together with their optimized fits. Under similar sample preparation conditions, the sample annealed at lower temperature generally shows higher O 1s intensity than that annealed at higher temperature. The O 1s intensity of samples prepared at UTC is higher than that of samples prepared at UNLV, especially for the metal oxides component. This is likely due to additional oxidation during transit from UTC to UNLV. The origin of increasing oxygen content can be addressed by carefully examining the Pt $4p_{3/2}$ feature, which also has two components: metallic Pt around 520 eV and Pt oxides around 524 eV. The ratio between these two components does not change more than 20% for the different samples, i.e., significantly less than the variation in oxygen intensity. Therefore, the increase of the O 1s intensity between samples prepared at the UTC and UNLV is interpreted as a result of oxidation of non-Pt metal components (likely Co in this case) and/or adsorption of oxygen-containing species on the carbon black during shipping. Furthermore, the O 1s spectrum from the sample annealed under vacuum has been obtained in situ at a base pressure of 5×10^{-10} mbar within two hours after the annealing process. Surprisingly, it shows a similar O 1s XPS intensity as the sample annealed under Ar flow (at higher annealing

temperature). This indicates that a reduction of the oxygen content in the annealing environment (i.e., vacuum vs. Ar flow) is helpful in reducing the oxygen content in/on the samples. However, even annealing in UHV is not sufficient to fully remove the oxygen from the samples.

On the theoretical side we investigated electronic structure, bonding, and hydrogen adsorption and desorption characteristics of several early transition metal clusters and their alloys with aluminum. Due to their high stability most of the calculations have been carried out on icosahedral clusters of Ti_{13} , Al_{13} , Sc_{13} , and Zr_{13} though larger 55 atom clusters have also been considered for Ti. It has been found that hydrogen saturation of these clusters with both icosahedral and octahedral geometries leads to multicenter hydrogen bonds (Figure 3(a) and (b)). These bonds are characterized by vibrational frequencies in the 1,100-1,500 cm^{-1} regime, which is quite distinct from vibrational frequencies associated with terminal hydrogen atoms on these metal clusters. One of the remarkable and novel features of hydrogen multicenter bonds is that the adsorbed hydrogen can be desorbed by vibrational excitation. While this has been experimentally demonstrated for desorption of molecular hydrogen from hydrogenated vanadium clusters and silicon surfaces, vibrational excitation could heat the metal clusters. However, mode-specific excitation could alleviate this problem and hence vibrational excitation of the infrared intense bands associated with hydrogen multicenter bonds may lead to desorption of the adsorbed hydrogen, enabling efficient reversible hydrogen storage. To gain mechanistic insights into the hydrogen adsorption process we are in the process of examining the transition states involved in the chemisorption reaction.

The calculations show that trace amounts of titanium dramatically alters the hydrogen binding capabilities of pure aluminum clusters, which might explain the role of titanium in the hydrogenation and dehydrogenation kinetics of complex metal hydrides. Figure 3(c) show the variation of the chemisorption energy with the composition of aluminum in $\text{Ti}_{13-n}\text{Al}_n\text{H}_{30}$ ($n=1-6,12,13$) clusters. Spurred by our recent findings that trace amounts of titanium in aluminum clusters dramatically enhance their ability to dissociatively chemisorb hydrogen, we explored the properties of several doped aluminum clusters. The choice of the dopant was dictated by experimental reports of the formation of alloys of these elements with aluminum. Our results indicate that hydrogen binding capabilities are dramatically enhanced by doping with iron or zirconium. This enhancement largely arises from the involvement of the d orbitals of the transition metal. Work is currently in progress to extend the findings of this study to other adsorbates like CO, O_2 , and H_2O that are present in fuel cell environments.

FIGURE 3. Optimized structures of (a) $\text{Ti}_{13}\text{H}_{30}$, (b) $\text{Al}_{12}\text{TiH}_{24}$ and (c) calculated chemisorption energies (ΔE_{CE}) of alloyed $\text{Ti}_{13-n}\text{Al}_n\text{H}_{30}$ ($n=1-6,12,13$) clusters.

We are also in the process of exploring the effect of an external electric field on hydrogen adsorption and saturation properties of transition metal clusters. Though there are extensive studies of interaction of small molecules with intense laser fields, there are no detailed experimental or theoretical studies of how hydrogen adsorption and desorption kinetics are modified in the presence of an external electric field. Our preliminary studies show that the effect of the electric field is to decrease the activation energy for hydrogen adsorption. This would also mean that the adsorbed hydrogen atoms can be desorbed at a lower temperature. This may have important consequences on hydrogen storage as well as catalytic properties of transition metal clusters as well as transition metal decorated nanostructures for hydrogen storage.

As part of the fuel cell membrane work, we prepared thin films of fluorine substituted sulfonated poly(ether amide)s (ODA-PFSA-xx and ODA-TFIPA-xx, where xx is the degree of sulfonation) and investigated their membrane properties. The fluorine substitution in the sulfonated polymers resulted in a significant reduction of water uptake level compared to that of non-fluorinated sulfonated polymers reported earlier. Even polymers with 90% sulfonation level (i.e., ODA-PFSA-90 and ODA-TFIPA-90) exhibited acceptable levels of water uptake (30–40 wt%). Accordingly, we were able to incorporate higher concentration of sulfonic acid moiety into the polymer and synthesize PEMs with higher ionic exchange capacity (ion exchange capacity = 1.7–2.1 mequiv/g). The fluorine substituted ODA-PFSA and ODA-TFIPA series ionomers showed higher conductivity than the non-fluorinated polymer, ODA-SCPA-70, and Nafion® when measured at 100% relative humidity and different temperature (see Figure 4). The highest conductivity was obtained from ODA-TFIPA-90 (207 mS/cm at 80°C).

To date we have successfully prepared aniline/Pd materials using two different synthetic methods. Two of the materials produced showed very high hydrogen sorption at room temperature. This fact is important. Unlike some of the sorption based hydrogen storage materials reported in the literature, these materials do not require liquid nitrogen temperatures to observe hydrogen sorption. We have spent the last quarter evaluating the reproducibility of the sorption/desorption of hydrogen for the two most promising polyaniline /Pd composites. Hydrogen sorption data is presented in Figure 5.

FIGURE 4. Proton conductivities of fluorine substituted sulfonated poly(ether amide)s and Nafion®.

FIGURE 5. Left: Hydrogen sorption at Aniline/Pd(ii) composite. Right: Percent hydrogen sorption at Aniline/Pd(ii) composite as a function of exposure time at desorption temperatures of 200°C and 160°C. Bottom: Hydrogen sorption/desorption isotherms for Aniline/Pd(ii) composite measure independently by Southwest Research Institute®.

The unsorbed hydrogen elutes in less than one minute with the sorbed hydrogen observed at ~3.5 minutes. In addition the exposure times do not result in large differences in sorbed hydrogen indicating fast kinetics. The adsorption/desorption isotherm for the composite is presented in Figure 5, bottom. This data shows maximum hydrogen sorption of 0.8% for the composite held at room temperature, as a function of equilibrium pressure. The results verify the sorption values obtained in our laboratory for the composite material. More importantly, the percentage of hydrogen sorption observed for the composite is the highest obtained at room temperature for any material in the literature to date.

Conclusions and Future Directions

Our studies of hydrogen adsorption on metal-decorated nanomaterials will be continued. One goal is to study the local morphology and electronic structure of Ti-decorated SWCNTs by using scanning tunneling microscopy and scanning tunneling spectroscopy. Furthermore, the influence of Ti and Li on the hydrogenation process will be studied by spectroscopy techniques at UNLV as well as with our new high-resolution photoemission setup at the Advanced Light Source (ALS) at Lawrence Berkeley National Laboratory. We hope to carry out theoretical studies to gain more insights into this as well as the role of alloying and external fields on hydrogen adsorption/desorption kinetics.

Pt₂IrCo supported by graphitized Vulcan XC-72 will be measured at ALS and UNLV. Their electronic structure, especially the valence and conduction band and the d-band structure will be compared to reference samples such as Pt, Co, and Ir metal.

Durability test of the new developed PEMs and incorporation of fluorine substituents into sulfonic acid moiety instead of polymer main chain are suggested.

FY 2009 Publications/Presentations

Presentations

1. I. Tran, R. Felix, Y. Zhang, M. Bär, C. Heske, and L. Weinhardt, "Microscopic and Spectroscopic Studies of Metal Deposition on Carbon Nanomaterials", with New Diamond and Nano Carbons Conference (NDNC 2009), June 7–11, Traverse City, MI (poster).
2. C. Heske, "How soft x-ray spectroscopy can shed light on the electronic and chemical properties of interfaces", ALS/CXRO Seminar Series, Lawrence Berkeley National Laboratory, Berkeley, May 13, 2009.
3. C. Heske, "How soft x-ray spectroscopy can shed light on the electronic and chemical properties of interfaces," PIRE-ECCI (Partnership for International Research and

Education) Seminar, Electron Chemistry and Catalysis at Interfaces, Department of Chemistry and Biochemistry, University of California, Santa Barbara, November 5, 2008.

4. C. Heske, "FCAST - The Fuel Cell and Storage Technology Project at UNLV", 2008 Annual Energy Symposium, UNLV, August 20, 2008.
5. C. Heske, "How soft x-ray spectroscopy can help the 'Hydrogen Economy' (hopefully)", Seminar Experimentelle Physik II, University of Würzburg, Germany, July 8, 2008.
6. R. Felix, I.C. Tran, L. Weinhardt, M. Bär, T. Hofmann, Y. Zhang, and C. Heske, "Study of the Interaction between Hydrogen and Carbon-based Nanomaterials", 2008 MRS Fall Meeting, Boston, Dec. 1–5, 2008 (Poster). Selected for Best Poster Award (\$500).
7. Y. Zhang, "The chemical and electronic structure of platinum-based nanoparticle catalysts for PEM fuel cells", 2008 American Chemical Society Western Regional Meeting, Las Vegas, Sept. 24–27, 2008 (Invited Oral).
8. T.S. Jo, C. Bae, "Synthesis of Ionic Conducting Polymers for Fuel Cell Applications and Biodiesel Productions" 42nd Western Regional Meeting of the American Chemical Society, Las Vegas, NV, September 23–27, 2008.
9. C. Bae, "New Functional Polymers for Alternative Energy Application" UNLV Renewable Energy Symposium, Las Vegas, NV, August 20, 2008.
10. Tarakeshwar Pilarisetty, Dhilip Kumar Thogluva Janardhanan, and N. Balakrishnan, Hydrogen storage and catalytic properties of transition metal clusters: Bonding changes and saturation effects, 236th American Chemical Society National Meeting, Philadelphia, PA, August 17–21, 2008.
11. T.J. Dhilip Kumar, P. Tarakeshwar, and N. Balakrishnan, Geometric and Electronic Structures of Ti-Al and Hydrogenated Ti-Al Nanoclusters, American Chemical Society Western Regional Meeting, Las Vegas, NV, September 24–28, 2008.
12. T.J. Dhilip Kumar, P. Tarakeshwar, and N. Balakrishnan, The Effect of Alloying on CO Tolerance of Pt Nanoparticles, American Chemical Society Western Regional Meeting, Las Vegas, NV, September 24–28, 2008.
13. Huy Mai, T.J. Dhilip Kumar, P. Tarakeshwar, and N. Balakrishnan, Computational Studies of H₂, O₂, and CO Adsorption on Pt and Pt-Ru Catalyst Clusters for Hydrogen Fuel Cell Applications, American Chemical Society Western Regional Meeting, Las Vegas, NV, September 24–28, 2008.

Publications

1. I. Tran, Dissertation, Department of Chemistry, UNLV: "Microscopic and Spectroscopic Studies of Metal Deposition on Carbon-based Materials", November 2008.
2. T.S. Jo, C.H. Ozawa, B.R. Eagar, L.V. Brownell, D. Han, and C. Bae, "Synthesis of Sulfonated Aromatic Poly(ether amide)s and Their Application to Proton Exchange Membrane Fuel Cells", *J. Polym. Sci., Part A: Polym. Chem.* **2009**, 47, 485–496.

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4. P. Tarakeshwar, T.J. Dhilip Kumar, and N. Balakrishnan, Hydrogen Multicenter Bonds and Reversible Hydrogen Storage, *J. Chem. Phys.* **130**, 114301 (2009).
5. T.J.Dhilip Kumar, P. Tarakeshwar, and N. Balakrishnan, Geometric and electronic structures of hydrogenated transition metal (Sc, Ti, Zr) clusters, *Phys. Rev. B* **79**, 022703 (2009).

IV.I.1 Novel Theoretical and Experimental Approaches for Understanding and Optimizing Hydrogen Interactions in Metal Organic Framework Materials

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Program Scope

In order to improve the gravimetric and volumetric capacities of metal organic framework (MOF) materials at room temperature beyond the 5 wt% and 40 g H₂/L, it is important to increase the H₂ binding energy above **20 KJ/mole**. This research aims to establish the scientific basis for such improvements by **i)** quantifying the interaction of H₂ molecules with MOF materials at room temperature to guide the synthesis of better storage MOF materials, **ii)** exploring H₂ loading kinetics and competitive impurity adsorption in practical environments over the 10 K-300 K temperature range, and **iii)** characterizing the effect of metal catalysts and associated spill over processes. To determine the H₂ binding energy, we have combined **high pressure infrared (IR) absorption, adsorption isotherms and isosteric heat of adsorption measurements** with a new first principles calculation method, the van der Waals density functional (vdW-DF), [1-3] to study a number of different MOF materials.

Recent Progress

1. Theoretical and Experimental Developments

During this past year, several issues were resolved to perform calculations on MOF structures:

1. By adopting the new computational algorithm of Roman-Perez and Soler [arXiv:0812.0244], we have achieved a many-fold efficiency enhancement allowing large van der Waals vdW-DF calculations to be done for large MOF systems at essentially the same rate as ordinary LDA or GGA calculations. This will be enabling greatly increased productivity, and has also enabled first principles structural relaxations with multiple dihydrogens within a MOF.

2. The exchange functional used with the vdW-DF has a history of giving spacings between H₂ and its surroundings that were a slightly too large. We have developed an improved method for exchange that better agrees with exact Hartree-Fock calculations, which is expected to fix this problem.
3. We are now able to treat not only the translational modes of H₂'s in a MOF, but also the rotational modes. For example, we can predict from first principles the spectra obtained from neutron scattering for the para-ortho transition at different H₂ loadings, including rather large and irregular triplet splittings and translational sidebands.

Experimental problems for IR absorption measurements have been identified and addressed as follows:

1. To avoid water contamination in the MOFs (affecting the IR spectra and competing with H₂ for available space), purification of H₂ gas was achieved by filters/hot H₂ gas cleaning of pipes.
2. Perturbation of MOF matrix by high pressure gas (due to modification of combination bands of the MOF in the H₂ stretch spectral region) was identified using He gas. A new procedure was established to acquire good quality data using D₂ as reference for H₂ measurements.
3. Both solvent and thermal activation of the MOFs prior to pressing them on KBr pellets was found to greatly improve H₂ loading. Alternative activation methods are being investigated as well.

2. Role of Organic Linkers and Structures in the Uptake and Binding Energy of H₂ in Microporous MOFs:

An initial effort was placed on **M₂(BDC)₂(TED)**, where M = Zn(**1**), Cu(**2**), Co(**3**) and Ni(**4**), BDC = benzenedicarboxylate, and TED = triethylene-diamine. These MOFs crystallize in the tetragonal crystal system, space group P4/ncc. The crystal structure is a 3D microporous framework composed of paddle-wheel M₂(COO)₄(TED)₂ secondary building units (SBUs), each linked by four BDC linkers and two TED pillars. The high resolution Ar and H₂ gas adsorption-desorption measurements were performed at various temperatures and pressures. The Ar sorption isotherms were collected in a relative pressure range from 10⁻⁶ to 1 atmosphere at 87K, and hydrogen sorption isotherms were collected in a pressure range from 10⁻⁴ to 1 atmosphere (low pressure) at 77 K and 87 K (e.g. Figure 1 for **1** and **2**), and from 10⁻⁴ to 40 bar (high pressures, not shown

FIGURE 1. (a) H_2 adsorption isotherms for 1 and 2 at 77 and 87 K. (b) Calculated isosteric heat of adsorption, Q_{st} , for both structures.

here). At 77 K and 1atm, the hydrogen uptakes are 2.1, 1.8, 2.13 and 2.08 wt% for 1-4. The uptake values are 4.1 and 3.5 wt% for 1 and 3 at 77 K and 40 bar, respectively. More details are summarized in Table 1.

TABLE 1. Pore Volume, Surface Area, H_2 Uptake and Q_{st} for Zn(1), Cu(2), Co(3), Ni(4)

M	Pore Vol (DA, cc/g)	Sur Area (BET, m ² /g)	H_2 , wt% (77 K, 1 atm)	Q_{st} (kJ/mol)
Ni(4)	0.74	1,783	2.08	5.0-6.0
Co(3)	0.83	1,881	2.13	5.0-5.7
Cu(2)	0.63	1,497	1.80	4.9-6.1
Zn(1)	0.84	1,888	2.10	5.0-5.3

The IR absorption of H_2 in $Zn_2(BDC)_2(TED)$, was measured by using D_2 as reference. Figure 2a (top panel) shows that the spectral region contains several components from overtone and combination MOF modes, which are affected by high pressure gas (see middle panel with D_2). By subtracting the spectrum obtained with D_2 at similar pressures, the H_2 stretch spectrum is reliably measured (Figure 2a bottom panel). There is a single mode centered at $4,120\text{ cm}^{-1}$ (composed of $3/4$ ortho- and $1/4$ para-hydrogen), i.e. located -35 cm^{-1} lower than the unperturbed ortho H_2 frequency ($4,155\text{ cm}^{-1}$). The intensity of this mode is linear

FIGURE 2. (a) IR absorbance of $Zn_2(BDC)_2(TED)$ at RT. **Top panel:** plain MOF at ambient pressure; **Middle Panel:** MOF at 800 psi H_2 (upper curve) and D_2 (lower curve); **Bottom panel:** Difference between H_2 and D_2 at several pressures for (a) $Zn_2(BDC)_2(TED)$ and (b) $Ni_2(BDC)_2(TED)$.

with pressure (Figure 3), as expected since the room temperature loading is still low ($\sim 10\%$ of maximum H_2 loading achieved at low temperatures).

The position of the H_2 mode in $Zn_2(BDC)_2(TED)$ and $Ni_2(BDC)_2(TED)$ is identical (Figure 2b), indicating that the corner metal atoms in these MOF do not play a role in H_2 loading. A similar H_2 vibrational frequency ($4,120\text{ cm}^{-1}$) was obtained upon loading ZIF-8, $[Zn_4(MeIm)_6]$, where (MeIm = methylimidazolate), a zeolite-like MOF, having different cage size and pore characteristics. Calculations are needed to understand this intriguing result.

The H_2 binding energy in $Zn_2(bdc)_2(ted)$ was mapped as a function of position. The deepest binding regions lie within channels of two types, A and B, whose position within the unit cell are indicated by the blue and brown lines respectively, where dashed circles indicate where the channels enter the respective adjoining cell, as shown in Figure 4.

The contour maps of these channels are shown in Figure 5 for channel A (left) and channel B (right). The fact that each of the strongest binding sites all have approximately the same binding energy of $\sim 10\text{ kJ/mole}$ is consistent with the experimental fact that the loading

FIGURE 3. IR integrated area of H_2 stretch for both MOFs and H_2 loading inferred from H_2 adsorption isotherms at RT

FIGURE 4. Unit cell

vs. pressure isotherms can be fitted precisely to a single Langmuir isotherm rather than a sum of two or more. Also, preliminary calculations indicate that little is changed for $M=Cu$ or $M=Co$.

Furthermore, we find that the MOF can be loaded with up to $\sim 12 H_2$ before H_2 repulsions begin to make each other addition more costly, in agreement with the isotherm-derived experimental number of ~ 13 . Our well-bottom values for the binding energy are reduced by zero point energies and thermal effects, which bring the net into reasonable agreement with the experimental isosteric heat of sorption. Finally we have calculated the shifts in the H_2 stretch frequency: at the strongest binding sites in each channel it is $\sim 30 \text{ cm}^{-1}$, which is in reasonable agreement with the measured $\sim 35 \text{ cm}^{-1}$. We are in the process of applying our recently developed hindered rotation analysis to this MOF. This is expected to bring the experimental and theoretical heats of sorption into nearly perfect agreement.

These results show that H_2 adsorption in $M_2(BDC)_2(TED)$ is due to the organic linkers and the channels are located away from high binding energy sites of each individual linker.

3. Frustrated Translational Motion in Smaller Restricted Channels in MOF

We have studied the $[M_3(HCOO)_6] \cdot DMF$ compounds, with $M = Co(5), Mn(6), Ni(7)$ that have very different ligands. The asymmetric unit contains four crystallographically independent $M(II)$ and six formate anions. This structure form one-dimensional zig-zag channels where the H_2 molecule can enter after removal of the DMF guest. The aperture of the channels is $\sim 5\text{-}6 \text{ \AA}$ roughly (excluded van der Waals radius), and the connection between channels exhibits a restriction.

The surface area was calculated to be $354 \text{ m}^2 \text{ g}^{-1}$ (Langmuir) and $304 \text{ m}^2 \text{ g}^{-1}$ (BET), respectively, in the

FIGURE 5. Channels A and B

pressure range of $7.94 \times 10^{-4} < P/P^\circ < 1.4 \times 10^{-2}$. The DA (Dubinin-Astakhov) micropore volume of the sample was $0.14 \text{ cm}^3 \text{ g}^{-1}$ based on the N_2 sorption data collected at 77 K. The main pore size was determined to be $\sim 5.0 \text{ \AA}$ from H-K pore size distribution with a good agreement with crystallographic data. Hydrogen uptakes were 0.75 and 0.65 wt% of at 77 K and 87 K and 1 atm, respectively. The isosteric heats of hydrogen adsorption (Q_{st}) were calculated to be in the range of 8.3-6.5 kJ mol $^{-1}$ at low coverage region (0.06-0.26 wt%).

Figure 6 shows the IR absorption data. Interestingly, the H_2 stretch vibration ($4,126 \text{ cm}^{-1}$) exhibits a smaller shift (lesser perturbation) than for the previous class of MOFs ($29 \text{ vs } 35 \text{ cm}^{-1}$), stressing again the role of the ligand. Furthermore, the spectra exhibit a distinct side band, centered at $\sim 4,040 \text{ cm}^{-1}$, which is assigned to the frustrated translation mode of the H_2 molecule. The sideband is detectable in this case, because of the constraint exerted by the restriction for H_2 molecules trapped in the channels.

4. A Path Towards Higher Binding Energies

The $\text{Zn}_2(\text{BPDC})_2(\text{BPPE})$, where *bpdc*=4,4'-biphenyldicarboxylate and *bppe*=1,2-bipyridylethene, is interesting because its structure is made of layers of two-fold interpenetrating $\text{Zn}(\text{BPDC})$ nets interconnected by BPPE that lead to the formation of unusual, high-binding energy sites. The Ar adsorption-desorption isotherms showed a typical Type I behavior. The surface area was estimated to be $328 \text{ m}^2/\text{g}$ (BET) and $483 \text{ m}^2/\text{g}$ (Langmuir), respectively. The total pore volume was calculated to be 0.165 cc/g . The IR absorption is characterized by a very sharp H_2 stretch at $4,117 \text{ cm}^{-1}$, i.e. with a higher binding energy than that of all previous MOF studied so far (Figure 7).

FIGURE 6. IR absorption spectra of H_2 in $\text{Ni}_3(\text{HCOO})_6$ and $\text{Mn}_3(\text{HCOO})_6$

Theoretically, the H_2 binding energy contours were mapped as a function of position in this MOF. These are shown in the primitive unit cell to the right. The binding is substantial at four sites shown ($\sim 15 \text{ kJ/mol}$), with four more equivalent sites in the upper pore of the cell. The strongest binding points are at the tips of each football shaped objects, and similarly in the other three large pores, yielding a total of 8 H_2 per primitive cell. This loading coincides with the loading where the experimental isotherms sharply break their slope and no longer increase sharply with pressure.

The calculations of the translational and hindered rotational zero point energies are not yet complete, but in analogy with previous MOFs we expect a net heat of sorption to be $\sim 11 \text{ kJ/mol}$, in rough agreement with the measurements. We have calculated the shift in the H_2 stretch frequency, which is $\sim 40 \text{ cm}^{-1}$ at the strongest binding sites, and $\sim 30 \text{ cm}^{-1}$ in the green regions in Figure 8.

FIGURE 7. IR absorption spectra of H_2 in $\text{Zn}_2(\text{BPDC})_2(\text{BPPE})$

Fig. 8

What have we learned about increasing H₂ binding in MOFs? Not including typical zero point and thermal reductions of up to ~5 kJ/mol, we can say the following:

The binding of H₂ to a single pi-aromatic structure (e.g. a benzene like ring) is **~5 kJ/mol**. In Zn₂(BDC)₂(TED) the binding is double this, as the strong binding sites in both channel A and channel B are near the strong binding points of two such pi structures, and the binding has increased to **~10 kJ/mol**. However, for Zn₂(BPDC)₂(BPDE), there are no less than four pi-aromatic complexes near each of the strong binding sites. Here the binding is **~15 kJ/mol**, and probably would be more if the complexes were more ideally situated. ***These findings suggest that we are close to the ultimate limit, i.e. energies in the 20 kJ/mol range could be achieved, so that MOF materials may prove suitable for practical storage devices.***

Current and Future Plans

Our spectroscopy effort will focus on i) low T measurements (10 K) to obtain a better comparison with theory at both low and high H₂ loading, and ii) addressing the spill over processes using a variety of model systems (MOF on catalytically active metal surfaces, small catalytic active nanoparticles deposited on MOFs, incorporation of catalytically active centers within MOFs).

Theoretically, we are considering the MOF-74, a material [4] that was recently [5] studied by inelastic neutron scattering at 4 K to sharpen our low temperature theoretical techniques for application to new MOFs created within our collaboration. The vdW-DF predictions were remarkably close to the experimentally measured positions of the 24 dihydrogens per cell. The most tightly bound one is found to have a binding energy of 12.5 kJ/mol, and with the translational and hindered rotational (see below) zero point energies this is reduced to 8.5 kJ/mol, in almost perfect agreement with the experimental values of 8.5 and 8.8 kJ/mol [5,6]. This contrasts with LDA and GGA values of 22 kJ/mol and 4.4 kJ/mol, respectively. The most exciting part of the story is the analysis of the **para-to-ortho transition**, where the experiment measured energy loss by scattering from different loadings of 100% para-H₂. The result is a series of loss peaks representing singlet to triplet transitions from the two most tightly bound types of H₂ sites, with the triplets split by the local potential energy contours. Using our *ab initio* energy contours, we solved the Schrödinger equation for the H₂ rotations for both types of site for various loadings, finding results agreeing with the experiment astonishingly well. As far as we know, **this is the first successful ab initio analysis of the hindered rotational spectrum of H₂ as function of H₂ loading in a MOF, or possibly in any other material.** The immediate impact

on the H-storage problem is a well tested method for including the non-negligible rotational zero point and excitation energies on heats of sorption.

Synthesis and high pressure hydrogen isotherms:

Based on the above findings, it is clear that structure components (e.g. ligands), crystal structures, pore size and shape play important roles in the amount of adsorbed hydrogen and binding energy. In general, smaller pore size, structure component with stronger hydrogen interactions, and larger number of binding sites will lead to higher isosteric heats of adsorption. The larger pore volume and internal surface area give rise to higher hydrogen uptake. Future synthesis will focus on optimized structures taking into consideration of these factors and incorporation of catalytical centers into the MOF structures via several mechanisms (e.g. spillover and metalloligands) to enhance MOF-hydrogen binding power. High pressure hydrogen isotherm measurements will be carried out on all newly synthesized MOFs at variable temperatures (up to 100 bar). The cryogenic (77 and 87 K) temperatures will be achieved using liquid nitrogen and liquid argon as coolant. A temperature controller unit will be used for temperatures ranging from 245 K to 425 K.

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6. W. Zhou, H. Wu, and T. Yildirim, J. Am. Chem. Soc. **130**, 15268 (2008).

1. Updated List of Awards

1. **Chabal**: 2009 Davisson-Germer prize (American Physical Society, March 2009).

2. Publications (acknowledging DOE support)

Hot papers:

1. "A luminescent Microporous Metal-Organic Framework for the Fast and Reversible Detection of High Explosives", Lan, A.J.; Li, K.H.; Wu, H.H.; Olson, D.H.; Emge, T.J.; Ki, W.; Hong, M.C.; Li, J. *Angew. Chem. Int. Ed.* **2009**, ASAP. http://www3.interscience.wiley.com/journal/26737/home/2002_hotpaper.html

Others:

1. “Theoretical and experimental analysis of H₂ binding in a prototypical metal-organic framework material”, Lingzhu Kong, Valentino R. Cooper, Nour Nijem, Kunhao Li, Jing Li, Yves J. Chabal, and David C. Langreth, *Phys. Rev. B* **79**, 081407(R) (2009).
2. “A Density Functional for Sparse Matter”, D.C. Langreth, B.I. Lundqvist, S.D. Chakarova-Käck, V.R. Cooper, M.Dion, P. Hyldgaard, A. Kelkkanen, J. Kleis, Lingzhu Kong, Shen Li, P.G.Moses, E. Murray, A. Puzder, H. Rydberg, E. Schröder, T. Thonhauser, *J. Phys.: Condens. Matter* **21**, 084203 (2009).
3. “Unique Gas and Hydrocarbon Adsorption in A Highly Porous Metal-Organic Framework Made of Extended Aliphatic Ligands”, Li, K.H.; Lee, J.Y.; Olson, D.H.; Bi, W.H.; Eibling, M.J.; Emge, T.J.; Li, J. *Chem. Comm.* **2008**, 6123.
4. “A Luminescent Microporous Metal Organic Framework for the Fast and Reversible Detection of High Explosives”, Lan, A.J.; Li, K.H.; Wu, H.H.; Olson, D.H.; Emge, T.J.; Ki, W.; Hong, M.C.; Li, J. *Angew. Chem. Int. Ed.* **2009**, ASAP.
5. “Microporous Metal Organic Frameworks as Functional Materials for Gas Storage and Separation”, Pan, L.; Li, K.H.; Lee, J.Y.; Olson, D.H.; Li, J. in *Design and Construction of Coordination Polymers*, John Wiley & Sons, Inc., in press.
6. “RPM3: A Multifunctional Microporous MOF with Recyclable Framework and High H₂ Binding Energy”, Lan, A.J.; Li, K.H.; Wu, H.H.; Kong, L.Z.; Nijem, N.; Olson, D.H.; Emge, T.J.; Ki, W.; Chabal, Y.J.; Langreth, D.C.; Hong, M.C.; Li, J. *Inorg. Chem.* **2009**, to be submitted.

3. Invited Talks at conferences (+ 17 at Universities not listed)

1. “Hydrogen storage in nanoporous materials”, Y.J. Chabal, American Physical Society, Pittsburgh, PA March 16-20, 2009.
2. D.C. Langreth, “International workshop: New achievement in density functional theory and quantum simulation of large systems”, Institute of Mathematics and its Applications, University of Minnesota, Minneapolis, August 2007.
3. D.C. Langreth, “International DOE workshop on Long range interactions in nanoscale science”, Annapolis, October 2007.
4. D.C. Langreth, Materials Research Society (MRS) meeting, San Francisco, March 2008.
5. D.C. Langreth, International workshop on Mathematical and Algorithmic Challenges in Electronic Structure, Institute of Mathematics and its Applications, University of Minnesota, Minneapolis, September 2008.
6. D.C. Langreth, DOE Workshop of the Computational Materials Science Network (CMSN) on Predictive modeling of the growth and properties of energy relevant thin film and nanostructures, Gatlinburg, October 2008.

7. D.C. Langreth, American Physical Society meeting, Pittsburgh, March 2009.
8. D.C. Langreth, Second International Symposium and Workshop on Correlated Electrons in Matter (ONRL & LLNL), Gatlinburg, April 2008.
9. D.C. Langreth, Kavli Institute of Theoretical Physics (KITP) program on Excitations in Condensed Matter: From Basic Concepts to Real Materials, Key participant, UCSB, Santa Barbara, November 2009.
10. V. Cooper, American Physical Society meeting, New Orleans, March 2008 V. Cooper, American Chemical Society National Meeting, New Orleans, April 2008.
11. V. Cooper, ES08, International workshop on Recent developments in electronic structure, Urbana-Champaign, June 2008 (Cooper).
12. V. Cooper, Gordon Research Conference on Computational Chemistry, Mount Holyoke, July 2008 (Cooper).
13. “Microporous Metal Organic Frameworks as Functional Materials for Gas Storage and Separation”, Jing Li, JeongYong Lee, Kunhao Li, Long Pan, David H. Olson, 5th National Symposium on Structural Chemistry, Fuzhou, P.R. China, October 27, 2007.
14. “Microporous Metal Organic Frameworks: Porosity and Multifunctionality”, Jeongyong Lee, Kunhao Li, Long Pan, David H. Olson, and Jing Li, 325th ACS National Meeting, New Orleans, LA, April 6–10, 2008.
15. “Microporosity and Functionality: An Update on MMOF Research”, J. Li, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian, China, July 11, 2008.
16. “Microporous Metal Organic frameworks: New Sorbent Materials for Hydrogen Storage”, J. Li, 4th Conference on Hydrogen Storage Materials, Guangzhou, P.R. China, April 11, 2009.

4. 14 Contributed Talks

5. List of people working on the project

In Chabal’s group, the work has been initiated by a research associate, **Jean-Francois Veyan**, who has worked on the project from the beginning with full funding. A student, **Nour Nijem**, has been training during the spring semester 2008 and is now being funded 100% by the grant, along with a new graduate student, **Kui Tan**, who has begun in Sept. 2008 and works on MOF synthesis. Chabal participates at the level of 2 months/year without support for summer salary.

In Langreth’s group, a postdoc (**Valentino Cooper**) started the theoretical effort. He was funded from an NSF account prior to arrival of DOE funds and for leveraging (budget too low to cover a full postdoc for three years). As of April 1, 2008, a new postdoc (**Lingzhu Kong**) has started and is being funded 100% by this DOE grant. Valentino Cooper stayed at 10-20% level until September 2008 to help with

the transition. David Langreth participates at the level of 2 months/year without support for summer salary.

In Li's group, Dr. **Kunhao Li** (postdoc) has been engaged in this research full time since the start of the program (August 2007). Two graduate students, **JeongYong Lee** and **Sanhita Pramanik**, have also been involved and partially supported by this program (1/2 time). Jing Li has been participating at the level of 1.5 months (academic year) and 0.5 month last summer without summer salary.

IV.I.2 Activation of Hydrogen Under Ambient Conditions by Main Group Molecules

Philip Power
University of California, Davis

DOE Grant Number ER46475,
The Regents of the University of California,
University of California, Davis,
Office of Research, Sponsored Programs,
1850 Research Park Drive, Suite 200,
Davis, CA 95616

Activation of Hydrogen Under Ambient
Conditions by Main Group Molecules
Principal Investigator: Philip P. Power
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Date of Report: April 6, 2009
Award Period: August 15, 2007 – August 14, 2009

Accomplishments:

A full paper describing the synthesis and characterization of a series of tin(II) hydrides by "chemical" reducing agents was published [1]. These have symmetrically bridged structures of formula $[(4-X-Ar')Sn(\mu-H)]_2$ ($4-X-Ar' = C_6H_2-4-X-2,6-(C_6H_3-2,6-Pr_2)_2$; $X = H, MeO, Bu^t$ and $SiMe_3$) or an unsymmetric hydride structure for the more hindered species $3,5-Pr_2-Ar'^*SnSn(H)_2Ar'^*-3,5-Pr_2$ ($3,5-Pr_2-Ar'^* = C_6H_3-2,6-(C_6H_3-2,4,6-Pr_3)_2-3,5-Pr_2$). The compounds were prepared either by direct reduction of the corresponding aryl tin(II) chloride precursors $ArSnCl$ with $LiBH_4$, Bu^tAlH (DIBAL) or via the reaction of $ArSnNMe_2$ with $BH_3 \cdot THF$. They were characterized by 1H , ^{13}C and ^{119}Sn NMR and Mössbauer spectroscopy. Calculations showed that the more hindering aryl groups favored the unsymmetric structure. It was also shown that the hydride Ar'^*SnH which is an orange colored, symmetric dimer in the solid phase has mostly an unsaturated structure and an intense blue color in solution owing to a change to the unsymmetric hydride structure and the existence of an equilibrium between the two forms.

Armed with the spectroscopic and structural data for a range of such hydrides we tested a different synthetic approach involving the direct reaction of H_2 with unsaturated tin precursors to see if the tin(II) hydrides could be produced by this approach. In addition, we decided to conduct parallel investigations

involving the direct reaction of NH_3 with the same compounds. The results are summarized in equations 1-3 [2].

25°C, 1 Atmosphere, $Ar' = C_6H_2-2,6-(C_6H_3-2,6-Pr_2)_2$

It can be seen that the reactions proceed under very mild conditions and the products **1-3** were isolated and essentially quantitative yield. They are the first examples of the direct reaction of the main group metals species with H_2 or NH_3 at 25°C and 1 atmosphere. The hydride and deuteride products **1** and **2** have symmetrically bridged structures. The reaction is remarkable in that $Ar'H$ or $Ar'D$ are also eliminated. Moreover, the reaction with deuterium (eq 2) shows that the deuterium is incorporated in the eliminated arene suggesting that the reaction proceeds through an $Sn(IV)$ intermediate in which H_2 or D_2 oxidatively adds to $SnAr'_2$ as shown by equation 4.

The reaction with ammonia (eqn 3) affords the amido bridged dimer **3** in quantitative yield also with arene ($Ar'H$) elimination. This reaction occurs below room temperature. The reactions are related to the addition of hydrogen or ammonia to stable carbenes reported recently by Bertrand [3].

The reaction of H_2 with a range of distannynes as shown in equations 5 and 6 was also investigated.

The reactions proceeded very smoothly to afford the products cleanly and essentially quantitative yield [4]

the reactions may be contrasted with our earlier results on the corresponding germanium species Ar'GeGeAr' with hydrogen which afforded a mixture of products $\text{Ar'(H)}_2\text{GeGe(H)}_2\text{Ar'}$ and Ar'GeH_3 in an approximately 2:1 ratio [5].

The direct reaction of hydrogen and ammonia with unsaturated group 13 metals was also investigated [6] the reaction of hydrogen or ammonia with the digallene Ar'GaGaAr' afforded the product shown in equations 7 and 8.

The yields in each case were quantitative and the products were characterized by ^1H and ^{13}C NMR and IR spectroscopy as well as by X-ray crystallography. The compounds were the first instance of hydrogen or ammonia addition to a main group 13 metal species.

The reactions described in equations 1-8 together with the earlier results suggest that the insertion of unsaturated main group molecules into N-N or N-H bonds is a general phenomenon. The exploration of the mechanisms and extent of such reactions will be investigated over the next year as outlined in Section 7.

References

1. Rivard, E.; Fischer, R.C.; Wolf, R.; Peng, Y.; Merrill, W.A.; Schley, N.D.; Zhu, Z.; Pu, L.; Fetting, J.C.; Teat, S.J.; Nowik, I.; Herber, R.H.; Takagi, N.; Nagase, S.; Power, P.P. *J. Am. Chem. Soc.*, **2007**, *129*, 16197-16208.
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4. Peng, Y.; Brynda, M.; Ellis, B.D.; Fetting, J.C.; Rivard, E.; Power, P.P. *Chem. Commun.*, **2008**, 6042-6044.
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6. Zhu, Z.; Wang, X.; Peng, Y.; Lei, H.; Fetting, J.C.; *Angew. Chem. Int. Ed.*, **2009**, *48*, 2031.

Publications

1. Rivard, Eric, Roland C. Fischer, Robert Wolf, Yang Peng, W. Alexander Merrill, Nathan D. Schley, Zhongliang Zhu, Lihung Pu, James C. Fetting, Simon J. Teat, Isreal Nowik, Rolfe H. Herber, Nozomi Takagi, Shigeru Nagase, and Philip P. Power. Influence of Steric and Electronic Factors on the Stability of Isomers of Divalent Tin(II) Hydrides: Experimental and Theoretical Studies. *Journal of the American Chemical Society*, **2007**, *129*, 16197-16208.
2. Yang Peng, Bobby D. Ellis, Xinping Wang and Philip P. Power, Diarylstannylene Activation of Hydrogen or Ammonia with Arene Elimination. *Journal of the American Chemical Society*, **2008**, *130*, 12268-12269.
3. Yang Peng, Marcin Brynda, Bobby D. Ellis, James C. Fetting, Eric Rivard, and Philip P. Power, Addition of H_2 to distannynes under ambient conditions. *Chemical Communications*, **2008**, 6042-6044.
4. Zhongliang Zhu, Xinping Wang, Yang Peng, Hao Lei, James C. Fetting, Eric Rivard, and Philip P. Power Addition of Hydrogen or Ammonia to a Low Valent Group 13 Metal Species at 25°C and 1 Atmosphere. *Angewandte Chemie International Edition*, **2009**, *48*, 2031-2033.

Personnel Supported

Hoppe, Elke	25% commitment through 4/30/09
Lei, Hao	GSR Summer-08 and GSR Winter-09
Ni, Chengbao	GSR July-08
Peng, Yang	GSR Summer-08
Power, Philip	1-wk summer commitment cost share
Wang, Xinping	100% commitment through 8/31/09

IV.I.3 Design and Synthesis of Novel Porous Metal-Organic Frameworks (MOFs) Toward High Hydrogen Storage Capacity

Principal Investigator: Mohamed Eddaoudi
Co-PIs: Michael Zaworotko and Brian Space (USF);

Sub-contracts: Ali Raissi (FSEC) and Juergen Eckert (UCSB)

Department of Chemistry, University of South Florida

Contract: DOE-BES ER46470

Project Start Date: 08/15/2007

Covered report period (August 15, 2008 to April 24, 2009)

Statement of Objectives:

1. Synthesize viable porous MOFs for high H₂ storage at ambient conditions to be assessed by measuring H₂ uptake.
2. Develop a better understanding of the operative interactions of the sorbed H₂ with the organic and inorganic constituents of the sorbent MOF by means of inelastic neutron scattering (INS, to characterize the H₂-MOF interactions) and computational studies (to interpret the data and predict novel materials suitable for high H₂ uptake at moderate temperatures and relatively low pressures).
3. Synergistically combine the outcomes of objectives 1 and 2 to construct a made-to-order inexpensive MOF that is suitable for super H₂ storage and meets the DOE targets.

The ongoing research is a collaborative experimental and computational effort focused on assessing H₂ storage and interactions with pre-selected metal-organic frameworks (MOFs) and zeolite-like MOFs (ZMOFs), with the eventual goal of synthesizing made-to-order high H₂ storage materials to achieve the DOE targets for mobile applications. We proposed in this funded research to increase the amount of H₂ uptake, as well as tune the interactions (i.e. isosteric heats of adsorption), by targeting readily tunable MOFs:

- 1)- Anionic open MOFs (i.e. ZMOFs) allow the addition of new sorption sites for H₂ in the void space (via post-synthesis modification aka ion exchange), an approach that is not feasible in neutral MOFs, and thus tunability of H₂ interactions by systematic evaluation of the extra-framework cations, a feature unique to anionic MOFs.

- 2)- Isorecticular compounds: a) allow the ability to easily modify the intra-framework constituents, assess their effect on H₂ sorption, and provide a direct comparison of the modified constituent(s) effects; our recently introduced *rht*-MOFs are excellent candidates for this method since *rht* is the only possible network for 3,24-connected nodes; b) permit systematic studies on the effect of pore volume on the amount of H₂ sorbed, since the ligands can be simply expanded while maintaining the same network topology.
- 3)- Model compounds can be used to assess the effect of pore size and functionality on H₂ sorption; molecular squares/boxes (MBs) are the systems of choice, because: a) they have been and can be synthesized from a variety of linkers (with myriad functionalities) and metals; b) to study the effects on H₂ sorption, their discrete nature and reduced unit cell (limited number of atoms) are ideally suited to molecular simulations studies; and c) the information gained from these MB systems can be implemented to design 3D MOFs (e.g. pillared 4.4 square grids, SGs) containing the desired attributes toward a material with strong H₂-framework interactions, an attribute suitable for storing H₂ at room temperature and moderate pressures.

Accordingly, we divided our research objectives into five subgroups: 1) Anionic MOFs (ZMOFs serve as the exemplary platforms) allow the facile exchange of extra-framework cations, where the impact of charge and/or polarizability on the isosteric heats of adsorption can be assessed; several ZMOF platforms have been synthesized with various metals and ligands. 2) The isorecticular system provided by the 3,24-connected *rht*-MOFs allows tuning of inorganic and organic components and permits to evaluate the effects of functionalization, pore size, and pore volume for direct and systematic comparison in a similar class of networks. 3) Molecular boxes allow for simplified studies on the effect of pore size and functionalization on H₂ sorption energetics. 4) We can expand the MB approach to generate open pillared 3D structures with a combination of small windows, high surface area, and large volume for higher uptake at higher pressures. 5) Computational studies allow us to elucidate the impact of each component on the energetics of sorption and predict novel materials to be made. The collaborative effort has a final objective of the eventual design and synthesis of an advanced material for super H₂ storage.

A. Description of Accomplishments

We have systematically investigated various strategies for substantial improvement of hydrogen binding energies in porous materials relative to those obtainable by simple physisorption in neutral MOFs or on carbons. This is being accomplished on several fronts, namely by the utilization of charged frameworks, reduction in pore size, tuning of pore geometries, incorporation of novel, open metal sites, and increases in the densities of the latter, as well as highly accurate and detailed computational studies on hydrogen interactions with porous hosts.

A.1. Anionic MOFs

- Demonstrated the remarkable tunability (pores size, charge density, surface area) of anionic ZMOFs.
- Carried out the first successful ion exchange in a MOF (similarly to what is routinely done in zeolites) using the *rho*-ZMOF framework, $[\text{Cation}^+_{48}][\text{In}_{48}(\text{C}_5\text{N}_2\text{O}_4\text{H}_2)_{96}]$.
- Ions (Li^+ , Mg^{2+}) exchanged were determined by single crystal X-ray diffraction to be hydrated and hydrogen-bonded to carboxylate oxygens, and are only indirectly accessible by H_2 .
- Isothermic heats of adsorption for hydrogen approaching 9 kJ/mol are achieved in these materials due to their high charge density.
- Synthesized a metal organic material (ME737) with extremely large cavities by incorporation of more than one appropriate organic functionality (two bridging organic ligands, 2-amino-4,6-PmDc and oxalic acid) along with yttrium. This novel ZMOF has a zeolite topology, thus far only encountered in inorganic materials. The structure consists of cages with an internal diameter of 38 Å. Each cage consists of 144 yttrium metal centers, representing one of the most hierarchical complex MOMs reported to date.

A.2. Effect of metal sites

- The effect of the intra-framework and extra-framework cations was investigated on the same platform namely sod-ZMOF. H_2 binding energies varied from 8 to 8.4 kJ/mol depending on the cation.
- Successfully synthesized the Fe analog of In soc MOF, which exhibits enhanced isosteric heat of adsorption for hydrogen at the metal site from 6.5 to 7.5 kJ/mol. An analog of In soc MOF with the more highly polarizable Cl instead of water in the axial position exhibited a slight increase in binding strength for hydrogen near the In to 7.2 kJ/mol.
- Demonstrated enhanced binding energies (<9.5 kJ/mol) and high gravimetric capacity

(2.4 wt% at 78K and 1 atm) in a unique compound $[\text{Cu}_6\text{O}(\text{TZI})_3(\text{H}_2\text{O})_9(\text{NO}_3)]_n \cdot (\text{H}_2\text{O})_{15}$ of *rht* topology with a high density of open metal sites, which occur in two types of clusters. The *rht*-like network is suitable for achieving higher surface areas and larger free pore volumes (isorecticular chemistry).

A.3. Effect of pore size; use of pillaring

- Reduction in pore size from 1.2 Å (PtS, topology) to 1.0 Å (Pth, topology) increases the average heat of adsorption for H_2 by some 20%, along with a similar increase in gravimetric capacity.
- Development of three-dimensional frameworks from two-dimensional pillared structures for assessing the effect of pore size and geometry on hydrogen storage.
 - Reduction in the pore size by changing the pillar in $\{\text{Zn}(\text{camphorate})(\text{bipy})_{0.5}\}_n$ from bipy (appr. 8x4 Å) to pyrazine (appr. 4x4 Å) increases the binding energy by 20% to more than 7 kJ/mol.

A.4. Computational Studies

- Constructed the first highly accurate, transferable hydrogen potential energy function from high-level ab initio calculations at the MP4 level of theory using correlation-consistent methods. Includes accurate orientational dependence of the potential energy interactions with explicit polarization.
- Calculated adsorption isotherms for H_2 in MOF-5 and soc MOF: show excellent agreement with experiment.
- Developed a supercomputing application, MPMC (Massively Parallel Monte Carlo) for sampling the Grand Canonical ensemble using techniques of statistical mechanical simulation.
- Demonstrated the effect of channel size on H_2 interaction energies by building up box of benzene molecules. Inclusion of additional benzene rings to enclose a single H_2 in an optimized box yields raises the interaction energies to near 13 kJ/mol from ~4 kJ/mol for a single benzene molecule.

B. List of Papers

Published

1. Nouar, F.; Eckert, J.; Eubank, J.F.; Forster, P.; Eddaoudi, M. "Zeolite-like Metal-Organic Frameworks (ZMOFs) as Hydrogen Storage Platform: Lithium and Magnesium Ion-Exchange and H-(rho-ZMOF) Interaction Studies" J. Am. Chem. Soc. 2009, 131, 2864-2870.
2. Liu, Y.; Kravtsov, V.; Eddaoudi, M. "Template-Directed Assembly of Zeolite-like Metal-Organic Frameworks

(ZMOFs): A usf-ZMOF with an Unprecedented Zeolite Topology” *Angew. Chem. Int. Ed.* 2008, 47(44), 8446-8449.

3. Nouar, F.; Eubank, J.F.; Bousquet, T.; Wojtas, L.; Zaworotko, M.; Eddaoudi, M. “Supramolecular Building Blocks (SBBs) for the Design and Synthesis of Highly Porous Metal-Organic Frameworks” *J. Am. Chem. Soc.* 2008, 130, 1833-1835.

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Submitted

7. Sava, D.F.; Kravtsov, V. Ch.; Eubank, J.F.; Eckert, J.; Eddaoudi, M. “Exceptional stability and high hydrogen uptake in hydrogen bonded Metal-Organic Cubes (MOCs) possessing ACO and AST zeolite-like topologies” *J. Am. Chem. Soc.* 2009.

C. List of People Working on the Project

In Year two, funds were requested in support of the equivalent of one full-time graduate student for each of three PIs located at USF, and one post-doctoral fellow. The following students were supported:

Student	type	months supported for the coverage dates of the present report
Amy Cairns	graduate	2.25
Dorina Sava	graduate	6.75
xFarid Nouar	graduate	4.50
John Perry	graduate	6.75
Jason Perman	graduate	2.25
Abraham Stern	graduate	4.50
John Belof	graduate	6.75
Dr. Xue Dong-Xu	post-doc	8.00

IV.I.4 Novel Molecular Materials for Hydrogen Storage Applications

P.I. Russell J. Hemley
Geophysical Laboratory,
Carnegie Institution of Washington

Contract Number: DE-FG02-06ER43280

Date of submission: 4/24/2009.

Covering the period 4/01/08 – 4/01/09.

Accomplishments:

1. Ammonia Borane – Rehydrogenation and Complexation at high P-T

Hydrogen interactions with NH_3BH_3 and its thermal residues have been investigated at pressures up to 10 GPa using in situ Raman spectroscopy in a Diamond Anvil Cell. At room temperature, pressure-induced complexation in the $\text{NH}_3\text{BH}_3\text{-H}_2$ system has been observed at 6.7 and 10 GPa. The formation of these complexes is accompanied by the appearance of vibrational modes shifted to a lower frequency at 5.7 GPa and to higher frequency at 10 GPa, relative to that observed in pure H_2 . In comparison to pure NH_3BH_3 , there are no noticeable changes to the internal modes of NH_3 and BH_3 functional groups in these complexes suggesting a close structural relationship to the corresponding high pressure phase of pure NH_3BH_3 . A likely origin of these intermolecular interactions is due to H_2 molecules that are stabilized by the dihydrogen bonding network in NH_3BH_3 . In another set of experiments conducted with thermal residues of NH_3BH_3 , i.e., polymeric aminoborane $[-(\text{NH}_2\text{BH}_2)_x]$ and polymeric iminoborane $[-(\text{NHBH})_x]$, it was found that H_2 preferentially complexed with these residues. The complexation was observed at pressures as low as 2 GPa at room temperature evidenced by the appearance of a broad low frequency H_2 stretching mode. Pressure-quenched complexes exist metastably at ambient conditions. This study has identified novel B-N-H complexes and established a complexation-based approach of hydrogen reuptake by chemical hydrides that could be extended to light metal complex hydrides as well.

2. Hydrogenation Studies in COF-102

The structural rigidity and behavior of COF-102 under pressure was explored using three different pressure media – silicone oil, Ar and H_2 by following the compressibility and deviation from cubic symmetry. The powder X-ray diffraction experiments performed

at the 16-ID-B beamline on samples of COF-102 supplied by the Yaghi group showed remarkable incompressibility in H_2 while the structure collapsed quickly at pressures below 1 GPa in other media. Using the data obtained from Ar and H_2 media, we estimate the amount of H_2 that can be packed into this material at high pressures and conclude that as much as 12 wt% of hydrogen storage can be effected using pressure. We also performed low temperature release experiments while monitoring the volume of the unit cell. The cell volume changes associated with H_2 release is observed to occur step-wise and complete at 59 K. Comparing the IR measurements on COF samples with and without H_2 indicates that there could be multiple sites of H_2 molecular adsorptions within the framework consistent with this observation of stepwise release. The H_2 vibron shows a decrease in frequency in comparison to that observed in pure H_2 and also shows a higher IR activity indicative of interaction between the framework and the adsorbed molecules rather than a purely pressure-induced packing.

3. Studies on the Silane-Hydrogen Binary System

Under high pressure conditions, methane (CH_4) was previously shown to form at least four stoichiometric van der Waals compounds with hydrogen (H_2). Recently, we have made significant progress in investigating interactions between molecular hydrogen and other group IVA covalent hydrides. We have demonstrated the formation of a novel compound of silane (SiH_4) and H_2 that displays markedly stronger intermolecular interaction than previously reported compounds. Vibrational spectroscopy of the new compound has revealed large H_2 binding energies that tend towards a “Kubas-like” state with pressure. These pressure induced interactions may be helpful in the design of novel storage materials with larger H_2 binding interaction.

4. $\text{Xe}_2(\text{H}_2)_{21}$ – A New Hydrogen-Rich Molecular Compound

Single crystal X-ray diffraction and optical spectroscopy measurements reveal the formation of a number of stable compounds in the Xe- H_2 binary system. At 4.8 GPa, a unique, hydrogen-rich, trigonal structure forms that can be viewed as a tripled solid hydrogen lattice modulated by layers of Xe, which in turn consists of xenon dimers. The structural refinements, based on new single crystal diffraction techniques, also provide clear evidence for pressure-induced changes in electron density associated with the formation of bonding states between xenon atoms and hydrogen molecules. Raman and infrared spectroscopy measurements reveal complex

interactions in this hydrogen-rich, van der Waals solid that is stable to pressures as high as 255 GPa.

5. Hydrogen Storage Studies in Crown Ethers

Crown ethers that form the backbone of supramolecular synthesis have been predicted to complex with H_2 molecules via the lone pair oxygens. There has been considerable interest in harnessing this interaction as well as the ability of crown ethers to form polymeric, transition metal-ion complexes to design new hydrogen storage materials. We have investigated the complexation of 12-crown-4; 15-crown-5 and 18-crown-6 with hydrogen at pressures up to 20 GPa and temperatures up to 600 K. In situ Raman and IR spectroscopy measurements indicate modulation of the C-O-C and H-H vibrational frequencies at pressures above 1.2 GPa indicative of active complexation. Surprisingly, larger pore size is observed to decrease complexation as observed from comparison of the pressures dependencies of vibrational frequencies in Ar, Ne and H_2 media. Low temperature release experiments in 15-crown-5 show that hydrogen is released in a single step at 160 K and can be efficiently replaced into the system at pressures as low as 0.2 GPa and 500 K.

6. Search for New Compounds in H_2 - H_2O System

The H_2 – H_2O system shows several stoichiometric compounds which may have potential for H_2 storage. Three high H_2 content compounds are currently known: sII clathrate (3.8 wt% H_2), filled ice C1 clathrate (1.8 wt% H_2), and filled ice C2 clathrate (10.1 wt% H_2). Exploration of new portions of the phase diagram may yield novel high energy content compounds. Recently, we made spectroscopic observations upon cooling samples of C1 and C2 clathrate indicating structural changes within the clathrate framework. As the samples were cooled, new features in both the rotational and vibrational spectra of H_2 suggest the presence of novel water environments hosting the H_2 molecules. These results may indicate a new low temperature clathrate structure which may have hydrogen storage implications.

Papers Published/Submitted

1. Pressure-Induced bonding and compound formation in Xenon and Hydrogen
Maddury Somayazulu, Przemyslaw Dera,

Alexander F Goncharov, Stephen A Gramsch, Peter Liermann, Wenge Yang, Zhenxian Liu, Ho-Kwang Mao and Russell J Hemley, *Science* (submitted).

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Research Personnel supported by this grant at the Geophysical Laboratory

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- (3) Qi Liang (1 month)

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IV.I.5 Bonding and Structures of Light Element-Hydrogen Systems under Extreme Conditions

PI: Wendy L. Mao

SLAC National Accelerator Laboratory &
Stanford University

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Period covered: January 2008-April 2009

Progress

Since the project began last year, we have been working on a number of high pressure experimental studies on hydrogen-rich light element phases to improve our understanding of the bonding and structures in these materials and their interactions with hydrogen. Notable progress in specific Group III-VI second row element systems are as follows:

H₂O & H₂O-H₂ system: We investigated the temporal, compositional, and compressional behavior of samples of H₂-H₂O, H₂O, and D₂O after X-ray irradiation. Unlike pure H₂O ice VII, C₂ which is hydrogen-filled ice Ic, did not dissociate in the presence of X-rays until 7 GPa. We collected data on the vibrational shifts of the new H₂-O₂ compound to 70 GPa and found that the behavior diverged from pure H₂ and O₂ with increasing compression. We are collaborating with Anders Nilsson's group to look at the structure of compressed H₂O using X-ray Raman. We conducted measurements at spectroscopy at SSRL beamline 6.2 on H₂O at 0.2 GPa in March 2009.

CH₄ and CH₄-H₂ system: We have been studying the high pressure behavior of pure CH₄ which we studied up to 200 GPa. We found that CH₄ remains in a cubic structure and as an insulator up the highest pressure studied. These results were published this month in *Chem. Phys. Lett.* We have initiated molecular simulations using the random generation of initial configurations approach which has been applied successfully to multi-component molecular systems to investigate the structure of CH₄(H₂)₄. A number of lowest energy configurations were found and they are the beginning input for the DFT calculations we are currently running. We are comparing these results with high pressure X-ray diffraction data on CH₄(H₂)₄ collected in December 2008. We looked at substituting carbon for the larger silicon as a means of chemical pre-compression to stabilize the CH₄(H₂)₄ structure to lower pressure. We studied the SiH₄-H₂ binary phase diagram at high pressure and ambient temperature,

and found that unlike CH₄-H₂ which has at least four stoichiometric crystalline phases, SiH₄-H₂ forms a simple eutectic.

Boron & Boranes: We investigated changes in the bonding of decaborane (B₁₀H₁₄) in a hydrogen-rich environment at high pressure using Raman spectroscopy. We found a transition at 3 GPa and a non-negligible amount of molecular H₂ dissolved in the decaborane at high pressure. This result is submitted to *J. Chem. Phys.* We studied the X-ray Raman spectra of amorphous and crystalline boron to 5 GPa. There appears to be a transition in the amorphous boron at 5 GPa, but we need high pressure data to confirm this result.

Ammonia: We collected XRS, XRD, and Raman spectroscopy on irradiated NH₃ for both fluid and solid phases at high pressure and found complicated radiation chemistry which we are currently analyzing (Figure 1). The incident 10 keV X-rays for XRS induced dissociation of NH₃, and we observed miscibility of H₂ and N₂ in the fluid phase at lower pressure and evidence for formation of a N₂-H₂ compound at higher pressure (7-8 GPa).

Ammonia borane: We investigated changes in bonding in ammonia borane (AB), NH₃BH₃ to pressures above 20 GPa using Raman spectroscopy, and found a number of phase transitions occur in over the pressure range studied which we plan to investigate using X-ray diffraction. The vibrational modes of the NH₃ proton donor group exhibited negative pressure dependence, consistent with the behavior of conventional hydrogen

FIGURE 1. Photomicrographs of NH₃ sample in a diamond anvil cell before and after exposure to ~10 keV X-rays. The darkened/cracked region shows where the beam passed through the sample and where we observed decomposition of NH₃ into a mixture of N₂ and H₂.

bonds, while the BH_3 proton acceptor group showed a positive dependence, supporting the presence of dihydrogen bonding at high pressure. This work was published in *J. Chem. Phys.* We have also looked at AB in the presence of excess hydrogen (H_2) pressure and discovered a solid phase, $\text{AB}(\text{H}_2)_x$, where $x \sim 1.3\text{--}2$. The new AB- H_2 compound can store an estimated 8–12 wt% molecular H_2 in addition to the chemically bonded H_2 in AB. This result is in press in *PNAS*. We have collected XRD on both pure AB and $\text{AB}+\text{H}_2$ to 20 GPa to look at the structural changes during these transitions.

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Personnel

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IV.I.6 Networks of Boron-Doped Carbon Nanopores for Low-Pressure Reversible Hydrogen Storage

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Reporting Period: August 15, 2008 – April 24, 2009

Program Scope

This project is an integrated synthesis/characterization/computational effort to develop novel materials – monolithic boron-doped carbon made from polymeric precursors, crisscrossed by networks of nanopores – expected to have superior hydrogen storage capacities not available in other materials. The aim is to develop a fundamental understanding of the mechanisms by which boron, through its electron-deficient electronic structure and long-range effect on distant carbon atoms, combined with appropriate pore geometries, creates deep potential wells which can hold films of physisorbed molecular hydrogen at densities much higher than undoped carbon. Such high-density films and their understanding at the molecular, statistical mechanical,

and macroscopic thermodynamic level are critical for the rational design of high-performance materials with controlled reversible storage characteristics at low pressure and room temperature. The project supports one of the high-priority research directions of the National Hydrogen Storage Project.

I. Recent Experimental Accomplishments

High Capacity Materials: Biocarbon, and Polymer-Based; Undoped and Doped with Boron

Various nanoporous carbons were analyzed for their potential to store hydrogen. Table I describes some of the systems analyzed, including two generations of undoped activated biocarbon (from corncob), two boron doped activated biocarbons, and three carbons based on synthetic polymers.

Figure 1 presents adsorption isotherms (80 K) for some of these samples. It is worth noting the significant increase in storage capacity of the new generation of activated carbons, 3K and 4K, vs. the older Batch 5.1. Sample 4K shows very high cryogenic storage capacity (14 wt% at 90 bar). Increasing the KOH-to-carbon ratio increases storage capacity (sample 4K vs. 3K), even though the surface area remains essentially the same. This suggests an increase of the fraction of high binding energy sites from 3K to 4K, by a mechanism yet to be understood. Early generations of polymer-based activated carbons (S7, S8, P11) show promise as hydrogen storage media, considering that some of them already show excess adsorption comparable to some of our best biocarbons. To normalize samples with different surface areas and pore volumes, we analyze H₂ uptake in terms of *areal excess adsorption* (gravimetric

TABLE I. High-Capacity Nanoporous Carbons

Sample	Description	Activation & Doping	BET Σ (m ² /g)	H ₂ excess ads. (g/kg @ 50 bar, 80 K)
3K	Biocarbon (corncob)	KOH:C = 3:1 (wt)	2,500	63
4K	Biocarbon (corncob)	KOH:C = 4:1 (wt)	2,600	73
Batch 5.1	Biocarbon (corncob)	KOH:C = 2:1 (wt)	3,100	44
3K-H7	Biocarbon, B ₁₀ H ₁₄ (liquid)	KOH:C = 3:1 (wt)	1,500	52
3K-H6	Biocarbon, B ₁₀ H ₁₄ (vapor)	KOH:C = 3:1 (wt)	2,400	68
S7	Pyrolysis of Saran (polyvinylidene chloride)	400°C (HCl release)	625	24
S8;0K-4B ^ b	Pyrolysis of Saran + K ₂ B ₁₂ H ₁₂	K ₂ B ₁₂ H ₁₂ , 790°C	N/A	34
P11;3K-5B ^ e	Pyrolysis of copolymer (polymethylene polyphenylisocyanate/Castor oil/H ₃ BO ₃ /epoxy oil) & KOH activation	Pyrolysis at 480°C; activation, with KOH:C = 3:1 (wt) at 790°C	N/A	60

FIGURE 1. Hydrogen adsorption isotherms for various carbon materials. Left: Total amount stored on boron-free biocarbons (precursors for B-doping with decaborane) activated with 3:1 and 4:1 ratios of KOH:C. Sample 4K reaches ~14 wt% at 90 bar and 80 K. Right: gravimetric excess adsorption for corn cob and polymeric precursors.

excess adsorption divided by BET surface area), which depends only on how strongly the surface adsorbs H₂ (but not on pore volume and surface area of the sample), and is a direct, (*p*, *T*)-dependent measure of the H₂ binding energy. Table II lists results for B-doped biocarbons. For B-free carbons, the highest areal excess adsorption at 50 bar and 80 K, 38 μg/m², is found for the polymer-based Sample S7, which is 36% higher than the best biocarbon value, 28 μg/m², for Sample 4K (see Table I). This is remarkable because it suggests that pore spaces can be engineered, toward high binding energies of H₂ on pure carbon, even more successfully than previously known (see Figure 2 and Ref. 1).

Boron Doping I: Liquid vs. Vapor Phase Deposition

Decaborane (B₁₀H₁₄) was identified as the most suitable compound for boron deposition onto high-surface-area, boron-free carbons. Decaborane is a stable crystalline solid, melts at 100°C, boils at 213°C (1 bar), and easily sublimates under moderate vacuum. With a molecular diameter of ~5 Å, it can easily reach all pores of interest in our biocarbon samples. At 200-250°C, it decomposes into nonvolatile hydrides, B_{10x}H_z, and H₂. Boron deposition occurs by the reaction

Three methods of carrying out the reaction were developed. In Method I (liquid deposition), B₁₀H₁₄ is deposited as a thin liquid film, followed by thermal decomposition of B₁₀H₁₄/B_{10x}H_z. In Method II (liquid-vapor deposition), a submonolayer of B_{10x}H_z is created by thermal decomposition of B₁₀H₁₄ liquid/vapor (admixed B₁₀H₁₄), followed by thermal decomposition of B_{10x}H_z. In Method III (vapor deposition), a submonolayer of B_{10x}H_z is created by decomposition of B₁₀H₁₄ vapor (sublimation of B₁₀H₁₄ in a separate chamber), followed by thermal decomposition of B_{10x}H_z.

Prompt gamma neutron activation analysis (PGNAA, ¹⁰B + *n* → ⁷Li + ⁴He + γ) at the University of Missouri Research Reactor is used to characterize the boron content of the doped materials, and areal excess adsorption was used to analyze the benefits of the different methods. Table II summarizes our results, including gravimetric and areal excess adsorption. Method I (liquid deposition) appears most efficient in delivering B, but reduces surface area, presumably by

TABLE II. Analysis of Samples Doped by Decaborane Decomposition

Sample (Method)	B:C (mix)	B:C (PGNAA)	BET Σ (m ² /g)	H ₂ gravim. excess ads. (g/kg @ 50 bar, 80 K)	H ₂ areal excess ads. (μg/m ² @ 50 bar, 80 K)
3K (precursor)	0	0	2,500	63	25
3K-H7 (I)	0.088	0.060	1,500	52	34
3K-H6 (II)	0.018	0.014	2,400	68	28
3K-H5 (III)	N/A	0.008	2,800	62	22

partial blocking of pores with B. Method II (liquid/vapor deposition) does not appear to block pores significantly and delivers a sizeable amount of B. Method III (vapor deposition) needs to be cycled to achieve significant doping. For a doping level of 6 wt%, a significant positive net effect of B-doping is observed: 3K-H7 has ~50% higher areal excess adsorption than 3K.

Boron Doping II: Copolymerization

The use of nanoporous biocarbon for B-doping – vs. fabrication of B-doped nanoporous carbon from boron-containing synthetic polymers – has been convenient because of the preexisting large surface areas in biocarbons. The results for doping with decaborane, in which the presence of boron in the activated carbons has been validated experimentally and the predicted increase in storage capacity per unit area with increasing boron content has been demonstrated, make a strong case that introduction of boron through synthetic polymers – copolymerization of carbon-carrying monomers and boron-carrying monomers – will generate materials with enhanced storage capacities. We have already fabricated several polymer-based carbons doped with boron by a variety of methods, with excess adsorption competitive with that of our best biocarbons (see Table I). Of particular interest is the unexpected result that Saran-based carbon, without boron, exhibits the highest areal excess adsorption observed in our laboratory (Sample S7 in Table I). Structural work on S7, to better understand this result, is presented in Figure 3. For the polymers with boron, work is in progress investigating how boron can be incorporated in the feedstock so that boron *substitutionally* displaces carbon in the final nanostructure (rather than forming patches or adatoms of boron), how different concentrations of boron (stoichiometric vs. non-stoichiometric) affect the electronic structure of the doped material and the associated functional implications for adsorption of H₂.

Hydrogen Binding Energy: Models for Adsorption

The nanoporous carbon storage capacities found so far have lead us to understand that a pore-space architecture that simultaneously maximizes gravimetric and volumetric storage capacities will likely consist of graphitic sheets that hold 2-3 layers of H₂ between adjacent sheets. Pore-size distributions from N₂ BET indicate the presence of pore sizes from sub-nm to several nm in width. Analysis of H₂ adsorption isotherms for various samples show that a two-binding-energy (BE) model for adsorption (narrow pores = large BE, wide pores = small BE) is adequate. (Figure 2; see also Section II.)

Characterization of Pores: Subcritical Adsorption of N₂ and Small-Angle X-Ray Scattering (SAXS)

Nitrogen adsorption isotherms from 10⁻⁷ to 1 bar at 77 K were measured for many carbons. Additional characterization was performed using SAXS. Figure 3 shows a N₂ adsorption analysis and SAXS analysis of the Saran-based carbon S7 (not doped, not activated with KOH, pores created by effluent HCl during pyrolysis) -[(CH₂)-(CCl₂)]- → 2C + 2HCl. The presence of mesopores is evident, but the bulk of the pore volume resides in micropores. The bimodal pore-size distribution is also seen in the SAXS spectrum.

II. Recent Theoretical and Computational Accomplishments

Quantum Rotors, Adsorption and a New Characterization Technique for Sub-nm Pores

Most simulations treat the molecules of H₂ as a point-like object (orientation unspecified), or at best consider a classical rigid-rotor model (2 angles). However, since hydrogen is so light the energy of rotational states is heavily quantized:

FIGURE 2. Absolute hydrogen adsorption for sample Batch 5.1. The surface area was 3,100 m²/g, with a nanopore volume of 0.76 cm³/g. Points are experimental. Left: single-BE fit, center: two-binding energy fit (75% of 4.8 kJ/mol, 25 % of 9.0 kJ/mol). Right: potentials of adsorption for various pore widths computed using Lennard-Jones potentials.

FIGURE 3. Left: N_2 adsorption isotherm for the Saran-based carbon S7 (boron-free). BET surface area is $625 \text{ m}^2/\text{g}$ with a total pore volume of $0.43 \text{ cm}^3/\text{g}$. Center left: pore size distribution from DFT analysis of the adsorption isotherm. Center right: SAXS spectrum for Sample S7. Right: SAXS analysis of S7 gives an average pore dimension of $6 \text{ Å} \times 6 \text{ Å} \times 17\text{-}24 \text{ Å}$ (broad minimum in χ^2) and surface area of $\sim 577 \text{ m}^2/\text{g}$, in good agreement with the BET area.

$$E_J = J(J+1) \frac{\hbar^2}{2\mu r^2},$$

with $(E_1 - E_0)/k_B = 175 \text{ K}$. Intuitively, it would appear that at low temperatures (e.g., 77 K) most H_2 molecules would remain in the $J = 0$ (spherical) state; however, the 9-fold degeneracy (nuclear spin + orbital) of the $J = 1$ state makes it relevant even at cryogenic temperatures. Intuitively, one would also expect quantum effects to be negligible at room temperature, but even at 300 K over 80% of the molecules are in the $J = 0, 1$ states (Figure 4).

We considered the interaction of H_2 in each of these states with the carbon adsorbent and with other H_2

FIGURE 4. Quantum rotational states of hydrogen molecules (amplitude of probability for the states s , p_x , p_y , and p_z).

molecules. The interaction potentials become matrices with indices corresponding to the different rotational states. Figure 5 shows samples of the potentials used for our calculations. The calculations improve the quality of the computer simulations (not shown here), and the solution of Schrödinger's equation for H_2 molecules in slit-shaped pores results in energy shifts for different rotational states, which can be probed via inelastic neutron scattering. Figure 5, right, graphs the center of the scattered intensity vs. pore width. For sub-nm sized pores this gives an attractive new characterization tool, which is most sensitive where other techniques (e.g., N_2 adsorption) lose their sensitivity. We are pursuing experimental tests of these predictions.

Effects of Boron Doping

Graphite does not bind hydrogen strongly (BE $\sim 5 \text{ kJ/mol}$). “Engineered” nanopores may raise the BE by a factor of 2: in very narrow pores, each H_2 sees the potential of both graphene layers. Computations performed by other groups predict that boron doping of carbon raises the BE of H_2 significantly, from $\sim 5 \text{ kJ/mol}$ to $15\text{-}38 \text{ kJ/mol}$, by charge transfer from the occupied σ

FIGURE 5. Hydrogen-graphene (left) and hydrogen-hydrogen (center) interactions for various rotational states. Right: $s \rightarrow p$ transition energies for H_2 molecules in slit-shaped nanopores vs. slit width.

orbital of H_2 to the empty pz orbital of B. In fullerenes, this generates strong-binding sites (~ 40 kJ/mol) (Ref. 7, Figure 3). In graphene, our calculations indicate a more modest increase, raising the BE from ~ 5 kJ/mol to ~ 8 kJ/mol, Figure 6.

Structural and energetic factors in designing a nanoporous sorbent for H_2 . The combined effect of boron doping and “pore engineering” should lead to BEs close to the ideal value ~ 15 kJ/mol for storage and delivery of H_2 at room temperature via pressure sweeps only. Figure 7 shows adsorption isotherms for a 1.08 nm pore at 77 and 298 K for two BEs (pure carbon, 5 kJ/mol, and doped ~ 15 kJ/mol). A boron-doped carbon appears capable of achieving the DOE targets for H_2 storage at room temperature. Figure 7 also shows the presence of multi-layer adsorption. This may explain the large adsorption of some of the samples (Section I). Future research directions: “ensemble” calculations of many boron-carbon configurations, determination of H_2 -substrate interaction for larger systems, consideration

of different geometries (small graphene platelets, non-substitutional boron doping, etc).

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FIGURE 6. Left: H_2 binding energy in boron-doped carbon (calculated at MP2 level). Center & right: 2.5, 5.0% of carbons were substituted randomly by boron. This raises the *average* BE by ~ 30 -50% over pure graphite.

FIGURE 7. Left: Hydrogen adsorption isotherms for pure carbon (binding energy ~ 5 kJ/mol) and boron-doped carbon (~ 15 kJ/mol). Center: density profile shows formation of a third layer of H_2 due to H_2 - H_2 interactions with the high-density first layers. Right: H_2 - H_2 interaction energy vs. pore width for multi-layer formation.

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IV.I.7 Elucidation of Hydrogen Interaction Mechanisms with Metal-Doped Carbon Nanostructures

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Savannah River National Laboratory
Contract Number: KC0201030
Fiscal Year 2008

Project Overview

This research work is aimed at obtaining a fundamental understanding of the nanoscale level of hydrogen sorption behavior of light-metal hydride material catalyzed by carbon nanostructures. The experimental work is closely linked to relevant modeling studies of these materials. Advances in hydrogen storage technology based on carbon nano-structures and particularly metal-doped carbon nanotube require the development of a basic understanding of their physicochemical properties and the manner in which these properties influence the hydrogen bonding. Our effort is focused on understanding of the hydrogen interaction mechanisms such as physisorption, weak covalent bonding, and chemisorption in these nano-carbon systems.

In the context of hydrogen, carbon nanomaterials have been commonly associated with use as storage materials. We have formulated a novel view; the employment of carbonaceous nanomaterials as catalysts for hydrogen uptake and release. The underlying mechanism relies on the electronegativity of the carbon-based nanomaterials (such as fullerenes and carbon nanotubes) which exerts a destabilizing effect on complex metal hydride systems by withdrawing electrons. The thus generated electron-deficient environment weakens the chemical bonds of hydrogen (e.g., the Al-H bond in NaAlH_4). This is a new concept on the catalysis of hydrogen storage reactions involving complex metal hydride materials. All currently considered catalysts (typically Ti or other transition metals) strongly react chemically with the host compounds, which complicates a thorough understanding of their catalysis mechanism.

Experimental work shows carbon nanostructure-catalyzed hydrogen uptake and release for sodium alanate (NaAlH_4) and lithium borohydride (LiBH_4). A survey of carbon material (fullerene, carbon nanotubes, and graphene) NaAlH_4 nanocomposites demonstrated varying degrees of catalytic activity. Partial reversibility of hydrogen was observed for NaAlH_4 and LiBH_4 . C_{60} materials were found to be

the best carbon additive for NaAlH_4 , rehydriding NaAlH_4 up to 4.3 wt% over 8 hours with 200 bar hydrogen overpressure. A fullerene- LiBH_4 composite demonstrates catalytic properties with not only lowered hydrogen desorption temperatures but regenerative rehydrogenation at a relatively low temperature of 350°C . C_{60} materials were found to be an excellent carbon additive for LiBH_4 , rehydriding LiBH_4 by 4.2 wt% over 12 hours with 120 bar hydrogen overpressure. We believe that a contributing factor to the performance of the C_{60} with both complex hydrides is its dispersibility.

This synergistic approach involving experiment and first-principles theory not only shows that carbon nanostructures can be used as catalysts for hydrogen uptake and release in complex metal hydrides NaAlH_4 and LiBH_4 , but also provides an unambiguous understanding of how the catalysts work. Interaction of NaAlH_4 with an electronegative substrate such as carbonaceous graphitic materials affects the ability of Na to donate its charge to AlH_4^- , consequently weakening the Al-H bond and causing hydrogen to desorb at lower temperatures as well as facilitating the absorption of H_2 to reverse the dehydrogenation reaction. Computation simulations show that the stability of NaAlH_4 originates with the charge transfer from Na to the AlH_4^- moiety, resulting in an ionic bond between Na^+ and AlH_4^- and a covalent bond between Al and H. Carbon nanostructures with zero, one, and two nanoscale dimensions (fullerene, carbon nanotubes, and graphene) show decreasing relative catalytic activity for hydrogen sorption in NaAlH_4 (see Figure 1). Based on our experimental observations and theoretical calculations

FIGURE 1. Correlation of the carbon substrate electron affinity and the hydrogen removal energy.

it appears the curvature of the carbon nanostructure plays a role in the catalytic process. This model provides a conceptual frame work for carbon nanostructure catalytic effects and a rational extension to a variety of complex hydrides.

The past years effort draws its strength from our synergistic approach, involving systematic experimental measurements complemented by state-of-the-art first-principles theory. This combination enabled us to demonstrate for the first time the surprising catalytic effect of carbon nanostructures on hydrogen uptake and release in sodium alanate and lithium borohydride, and at the same time, to reveal the mechanism at the atomic and electronic level that allows the carbon nanostructures to act as efficient catalysts in this system.

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IV.I.8 Kinetics and Thermodynamics of Metal and Complex Hydride Nanoparticles

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Accomplishments

Predicted New Ground State and Polymorphism of Mg Borohydride

In collaboration with Eric Majzoub (UMSL), we have developed a method which can predict entirely new, unsuspected ground state structure types for complex ionic crystals. Physically, this approach is based on the observation that complex hydrides are characterized by an arrangement of positively charged cations (e.g., Mg^{2+}) and negatively charged complex anions (e.g., BH_4^-), with strong covalent bonds within each anionic complex and predominantly electrostatic interactions between the cations and anions. These considerations suggest that the type and symmetry of the ground state crystal structure can be determined by minimizing the total electrostatic energy for a given set of ionic charges, ionic radii, and fixed shapes of complex anions. The resulting ground states, henceforth called *prototype electrostatic ground states* (PEGS), are then used as input to DFT calculations to relax all structural parameters and obtain accurate total energies. In [1] we showed that this method can successfully predict the observed ground states of alkali and rare earth aluminates, including currently unknown structures of several bi-alkali hexa-aluminates, such as LiCaAlH_6 , NaCaAlH_6 , KCaAlH_6 , NaMgAlH_6 , and KMgAlH_6 . Using the PEGS search strategy, we have predicted a new $T=0$ K ground state of $\text{Mg}(\text{BH}_4)_2$ of tetragonal $I\bar{4}m2$ symmetry (see Figure 1), which is lower than all other previously

predicted structures. Interestingly, it is also 5 kJ/mol lower in energy than the recently proposed $P6_1$ structure with 30 formula units per primitive cell. Our predicted structure represents a truly new prototype that has not been observed in any other systems, and demonstrates the effectiveness of the PEGS method. The calculated thermodynamic properties of magnesium borohydride are found to be ideal for reversible storage: its enthalpy $\Delta H=29.5$ kJ/(mol H_2) and entropy are $\Delta S=101$ J/(K mol H_2) for the thermodynamically favored decomposition pathway into $\text{MgB}_{12}\text{H}_{12}$, MgH_2 , and H_2 .

Hydrogen Storage in Li-Sc-B-H

In collaboration with Eric Majzoub (UMSL) and experimentalists from Caltech/JPL [2], we have conducted an in-depth study of crystal structures and thermodynamic properties of borohydrides with Li^+ and Sc^{3+} cations. For $\text{LiSc}(\text{BH}_4)_4$, a tetragonal structure in space group $I\bar{4}$ (#82) was predicted to be significantly (60 kJ/mol) lower in energy than the $P\bar{4}2c$ structure proposed from high-resolution X-ray data [3]. The predicted diffraction patterns of $I\bar{4}$ do not correspond to those obtained from crystalline ternary borohydride phases made by ball milling, suggesting that several metastable polymorphs may exist. Our thermodynamic calculations show that $\text{LiSc}(\text{BH}_4)_4$ is stable at low temperatures. We find that the formation energy for reaction, $\text{LiBH}_4 + \text{Sc}(\text{BH}_4)_3 \rightarrow \text{LiSc}(\text{BH}_4)_4$, is strongly

FIGURE 1. New low-energy $I\bar{4}m2$ structure of $\text{Mg}(\text{BH}_4)_2$ predicted using Monte Carlo electrostatic energy optimization [1].

negative, $\Delta H = -30$ kJ/mol at $T = 27^\circ\text{C}$, indicating that this compound readily forms upon ball-milling. Hydrogen release from $\text{LiSc}(\text{BH}_4)_4$ is predicted to occur via a series of steps:

Since hydrogen release from borohydrides typically has high kinetic barriers and requires temperatures of at least a few hundred $^\circ\text{C}$, it is likely that the first two steps will remain “kinetically frozen” until the temperature of the third step ($+170^\circ\text{C}$). Thus, the formation of LiBH_4 may be by-passed altogether and the decomposition process may go directly into $\text{Li}_2\text{B}_{12}\text{H}_{12}$, LiH , ScB_2 , and H_2 , in good agreement with experimental data.

In addition to $\text{LiSc}(\text{BH}_4)_4$, we have predicted the currently unknown crystal structures of $\text{Sc}(\text{BH}_4)_3$ and $\text{Sc}_2(\text{B}_{12}\text{H}_{12})_3$ (see Figure 2); the former is marginally unstable at $T = 0$ K w.r.t. hydrogen release, while $\text{Sc}_2(\text{B}_{12}\text{H}_{12})_3$ is predicted to be thermodynamically stable up to $T_c = 214^\circ\text{C}$ at 1 bar H_2 pressure. Overall, we conclude that the Li-Sc-B-H system is not an attractive candidate for hydrogen storage.

New Entropically Optimized Hydrogen Storage Reactions in Li-Mg-Ca-B-H

Metal borohydrides [LiBH_4 , $\text{Mg}(\text{BH}_4)_2$, $\text{Ca}(\text{BH}_4)_2$] are attractive candidates for onboard storage because they contain high densities of hydrogen by weight and by volume. We have applied the recently developed prototype electrostatic ground state (PEGS) search method [4] and the DFT-based grand-canonical linear programming approach (GCLP) [5] to predict currently

FIGURE 2. Left panel: Orthorhombic $C222$, crystal structure of $\text{Sc}(\text{BH}_4)_3$. Right panel: Planar projection of the predicted Cm crystal structure of $\text{Sc}_2(\text{B}_{12}\text{H}_{12})_3$. Semitransparent yellow plane marks the (001) lattice plane, Sc^{3+} ions are violet, and $[\text{B}_{12}\text{H}_{12}]^{2-}$ groups are cyan.

unknown crystal structures and hydrogen storage reactions in the quinary Li-Mg-Ca-B-H system. We show how the *combination* of these two methods provides a powerful theoretical framework for predicting new high capacity hydrogen storage reactions with excellent thermodynamic properties. In particular, we use PEGS to predict the crystal structures of $\text{X}_n\text{B}_{12}\text{H}_{12}$ compounds. For $\text{LiB}_{12}\text{H}_{12}$, we find a new phase of $C2/m$ symmetry that is 7 kJ/mol lower in energy than the recently proposed $Pa\bar{3}$ phase obtained in solution-grown samples of $\text{Li}_2\text{B}_{12}\text{H}_{12}$ [6]. For $\text{MgB}_{12}\text{H}_{12}$ and $\text{CaB}_{12}\text{H}_{12}$ we propose crystal structures of $C2/m$ and $C2/c$ symmetry, respectively. We find that LiBH_4 and $\text{Mg}(\text{BH}_4)_2$ are thermodynamically favored to release H_2 by forming $\text{Li}_2\text{B}_{12}\text{H}_{12}$ and $\text{MgB}_{12}\text{H}_{12}$, respectively, while $\text{Ca}(\text{BH}_4)_2$ has two thermodynamically degenerate decomposition pathways, one of which involves an intermediate $\text{CaB}_{12}\text{H}_{12}$ phase, while the other goes directly into CaB_6 and CaH_2 . Surprisingly, we also find that the classical destabilized $\text{LiBH}_4 + \text{MgH}_2$ reaction is thermodynamically favored to proceed via an intermediate $\text{Li}_2\text{B}_{12}\text{H}_{12}$ compound.

More importantly, we predict two new and previously unsuspected reactions (see Table 1), belonging to a qualitatively new class of entropically optimized reactions that use fully hydrogenated high-entropy borohydrides as reactants and lead to the formation of low-entropy $\text{X}_n\text{B}_{12}\text{H}_{12}$ phases as end products. Low reaction enthalpies [~ 25 kJ/(mol H_2)], which should significantly simplify heat management during on-board recharging, are compatible with nearly ideal thermodynamics (hydrogen release is predicted to occur around -20°C at $p = 1$ bar H_2 pressure) due to the exceptionally low vibrational entropies of the $\text{Li}_2\text{B}_{12}\text{H}_{12}$ and $\text{CaB}_{12}\text{H}_{12}$ product phases. We formulate a guideline for designing new complex hydride reactions with *low entropies* – use reactants that have complex anions constituted by a small number of atoms (such as NH_2 , BH_4 , etc., resulting in a high number of low frequency phonon modes per atom) and products that are either tightly bound bulk phases or materials with large complex anions (e.g., $\text{B}_{12}\text{H}_{12}$), exhibiting few low-frequency phonon branches. Low entropies have a highly beneficial effect since they allow the use of materials with lower reaction enthalpies while

FIGURE 3. Predicted crystal structures of $\text{Li}_2\text{B}_{12}\text{H}_{12}$ (left) and $\text{MgB}_{12}\text{H}_{12}$ (right) See ref. [7].

TABLE 1. Predicted new hydrogen storage reactions for borohydrides. Enthalpies and entropies are given in kJ/(mol H₂) and J/(K mol H₂), respectively. ΔH^{300K} are the calculated enthalpies at T = 300 K, including vibrational energies. T_c gives the temperature of hydrogen release at p = 1 bar of hydrogen pressure.

Reaction	Wt% (kg H ₂ /kg)	Vol. density (g H ₂ /l)	ΔH^{300K}	ΔS^{300K}	T _c (°C)
5Mg(BH ₄) ₂ + 2LiBH ₄ → Li ₂ B ₁₂ H ₁₂ + 5MgH ₂ + 13H ₂	8.4	46 (64)	24.4	100.0	-29
5Mg(BH ₄) ₂ + CaBH ₄ → CaB ₁₂ H ₁₂ + 5MgH ₂ + 13H ₂	7.7	51 (70)	25.7	100.5	-18

maintaining the same equilibrium H₂ pressure. Other things being equal, lower enthalpy reactions are always better due to a smaller amount of heat released during exothermic regeneration of these hydrides. These results demonstrate the power of the combined theoretical framework for structure prediction and linear programming-based reaction prediction, showing that previously unsuspected reactions can be found even in extensively studied materials systems.

Crystal Structure and Phonon Instability of High-Temperature β -Ca(BH₄)₂

Ca(BH₄)₂ is an interesting candidate for high-density hydrogen storage since it contains a large amount of hydrogen by weight and volume, and has been shown to reversibly release and absorb hydrogen, albeit at moderately high temperatures. Ca(BH₄)₂ undergoes a polymorphic transformation around 400–440 K from a low-temperature α -Ca(BH₄)₂ phase to a high-temperature β -Ca(BH₄)₂ phase. The crystal structure of β -Ca(BH₄)₂ has only recently been resolved, and its thermodynamic phase stability is still not well understood. Using a combined experimental and theoretical approach, we have independently determined the structure of β -Ca(BH₄)₂ and assessed its thermodynamic stability in the quasiharmonic approximation. The space-group *P42/m* gives an excellent agreement between experiment and theory, confirming the result of a recent study [Buchter *et al.*, J. Phys. Chem. B **112**, 8042 (2008)]. Using density-functional theory (DFT), we obtained a value of 10.9 kJ/mol for the static total-energy difference between the α -Ca(BH₄)₂ and the β -Ca(BH₄)₂ phases at T = 0 K (without vibrations). Using DFT linear-response calculations, we find that the $[\frac{1}{2} \frac{1}{2} \frac{1}{2}]$ acoustic phonon branch of β -Ca(BH₄)₂ is dynamically unstable on the Brillouin-zone boundary at the T = 0 K lattice parameters predicted from static DFT calculations. This phonon branch is very sensitive to the lattice parameters and can be stabilized by including lattice expansion due to zero-point vibrational contributions in the quasiharmonic approximation. This expanded stable β -Ca(BH₄)₂ structure has a room-temperature vibrational entropy that is 16 J/mol K higher than that of the α -Ca(BH₄)₂ phase, qualitatively consistent with the observed stabilization of the former at elevated temperatures. The main contribution to the entropy difference between the α -Ca(BH₄)₂ and β -Ca(BH₄)₂ phases comes from the

low-frequency region dominated by translational and rotational phonon modes.

First Principles Molecular Dynamics Study of the Structure and Dynamic Behavior of Liquid Li₄BN₃H₁₀

Recent experimental and computational studies have shown ‘complex hydrides’ to be promising hydrogen storage materials. Some of these materials are known to release hydrogen from the liquid state, such as Li₄BN₃H₁₀, however no experimental nor computational studies on its liquid structure have been reported. We have applied density functional theory based ab initio molecular dynamics to examine Li₄BN₃H₁₀ at temperatures both above and below the experimental melting point [8]. We examined the structure of the liquid, vibrational spectra, diffusivity and compared to experiments and the solid state. We found that the liquid state, like the solid state, is a mixture of Li⁺, BH₄⁻ and NH₂⁻ with ionic interactions between the BH₄⁻ and NH₂⁻ anions and the Li⁺ cations; however, the liquid demonstrates wide bond angle distributions in the anionic units, indicating that these units are not merely rigid. Our study also found that the Li⁺ sub-lattice disorders more readily than the other species. We calculated the activation energy and pre-exponential factor for Li⁺ diffusivity to be ~20 kJ/mol

FIGURE 4. (a) Phonon dispersion of β -Ca(BH₄)₂ at the static total-energy minimum. Negative values correspond to unstable phonon branches with imaginary frequencies. (b) The same as (a), but after 2% expansion along the a and b lattice parameters, and 1% expansion along the c lattice parameter. Note that the instability vanishes for this geometry.

and 15×10^4 cm²/s, respectively. Finally, by computing the power spectrum, we find that the liquid contains the major internal vibrational modes of the solid, however the low frequency modes become more prominent with increasing temperature.

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8. D.E. Farrell, A. Thompson, D. Shin, and C. Wolverton, “*First Principles Molecular Dynamics Study of the Structure and Dynamic Behavior of Liquid Li₄BN₃H₁₀*,” (in preparation, 2009).

Publications

1. C. Kim, S.-J. Hwang, R.C. Bowman, Jr., J.W. Reiter, J.A. Zan, J.G. Kulleck, H. Kabbour, E.H. Majzoub, and V. Ozolins, “*LiSc(BH₄)₄ as a Hydrogen Storage Material: Multinuclear High Resolution Solid State NMR and First-Principles Density-Functional Theory Studies*,” to appear in *Journal of Physical Chemistry C* (2009).
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IV.I.9 Atomistic Transport Mechanisms in Reversible Complex Metal Hydrides

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directly to *density-functional theory (DFT) and atomistic modeling*, and thus allows an unprecedented level of interaction between experiment and theory. Key questions addressed via combined experimental and theoretical efforts include:

- The mechanisms by which a Ti catalyst facilitates H₂ dissociation, a key initial step in the reaction transforming metallic Al to Al-H species and, ultimately, to a complex hydride.
- The fundamental factors determining the formation and diffusion kinetics of alanes, which we have identified as primary carriers of mass transport during hydrogenation.
- The possibility that kinetic bottlenecks in the hydrogenation reaction could be circumvented by tailoring the reaction environment, thus allowing the facile hydrogenation of previously irreversible materials.

Program Scope

The development of materials for efficient hydrogen storage has been recognized as a major obstacle on the way to a hydrogen economy. Most solid-state hydrogen storage materials, for instance, cannot be cycled reversibly between H-rich and depleted phases and exhibit slow reaction kinetics. Dopants and catalysts, nanostructuring, and finely tuned reaction environments could provide improved properties.

This research project aims to establish a scientific basis for such improvements in two interlinked thrusts: (i) development of a comprehensive understanding of the fundamental, atomic-scale mechanisms underlying the facile reversible H storage in titanium-doped sodium aluminum hydride (NaAlH₄), one of very few known complex hydrides allowing *reversible hydrogen storage with fast reaction rates*. And ii) Utilization of this basic knowledge for the development of new reversible H-storage materials with high storage capacity and fast reaction kinetics.

We consider the *hydrogenation reaction*, proceeding from a H-depleted phase (NaH and metallic Al) via Na₃AlH₆ to the H-rich NaAlH₄, as the basis for understanding reversible H storage, and in particular dopant and catalyst effects. Surface processes are expected to be of central importance. In contrast to previous research on bulk compounds with complex reaction pathways, microstructures, and unknown impurity concentrations, the present program emphasizes the use of *well-defined model systems* and of *state-of-the-art surface experiments* to achieve a quantitative understanding of the important reaction mechanisms. This approach is generating data accessible

The long-term goal of this project is to develop an atomistic understanding of the interaction of hydrogen with metal, metal alloy, and alkali metal surfaces as well as nanostructures, hence providing a scientific basis for solid-state hydrogen storage in support of the DOE BES hydrogen fuel initiative.

Recent Progress

1. Role of Ti in Enabling Reversible Hydrogen Storage in Complex Hydrides

Following our theoretical prediction that specific atomic Ti complexes on Al surfaces efficiently dissociate H₂ adsorbing from the gas phase (a crucial first step in the hydrogenation reaction) [4,5], and having studied the formation of such complexes by combined atom-resolved scanning tunneling microscopy (STM) and DFT [9], atomic-resolution microscopy was used to establish how hydrogen interacts with Ti-doped Al surfaces [21]. These recent studies resulted in the following main findings:

- Kinetic barriers slow the dissociation of adsorbing H₂ sufficiently to make it impractical to observe H₂ dissociation near Ti at low H₂ pressures typically accessible to STM. We have thus developed an elevated pressure STM capability extending the operating range to at least 10 torr while maintaining impurity levels near 10⁻¹⁰ torr. This new experimental capability is now being used for atomic-resolution studies of hydrogen-metal interactions near practically relevant conditions.
- Combined STM imaging and DFT were used to establish the interaction of atomic H with

FIGURE 1. (a) Identification of H-binding sites by STM imaging (top) and DFT-based image simulation for second-nearest neighbor Ti-Ti pairs on Al(111), with and without a H-atom in different sites (bottom). (b) Kinetic Monte Carlo simulation of H-atom diffusion near Ti/Al(111) at room temperature, showing the transient trapping of H near Ti atoms. (c), (d) Potential energy surfaces for a H-atom on Al(111) and Al(100), respectively.

dispersed Ti on Al(111). Individual H atoms near surface Ti dopants were identified by STM, and followed by time-lapse STM over extended time periods (Figure 1a) [21]. Combined with ab-initio calculations and kinetic Monte-Carlo (KMC) simulations, these experiments have identified *specific binding sites for H atoms*, and have demonstrated that H can easily *diffuse onto all-Al surface sites*, thereby regenerating the catalytic Ti complex and allowing further H₂ dissociation.

- In an effort to develop a comprehensive theoretical understanding of H storage processes, we combined DFT with KMC simulations to use atomic-level information in determining the behavior of the system over much larger length and time scales. As a first application, we have elucidated the diffusivity of different species (H, Al, Al_xH_y) on Ti-doped Al(111). Shallow potential wells around embedded Ti atoms transiently trap H and reduce its diffusivity (Figures 1b-d), but not that of the other species. This effect has important consequences on hydrogenation reactions in the presence of Ti dopants. Unexpectedly, Al and alane (Al-H) species diffuse much faster than H; and the rate of mobile alane formation is slowed considerably,

since it involves the rather slow “harvesting” of H by diffusing Al.

- In the second phase of our computational studies, we compared the diffusivities of H and alane species on two different Al surfaces: Al(111) and Al(100). Embedded Ti atoms create potential wells for H atoms in both surfaces (Figures 1 c, d), but the well is significantly deeper on Al(100) [0.72 eV] than on Al(111) [0.45 eV]. The diffusivity of alanes is higher on Al(111) than on Al(100), primarily due to differences in surface corrugation. The enhanced diffusion of all species on Al(111) is contrasted by the much lower activity in H₂ dissociation of the (111) surface. While there is a 0.7 eV dissociation barrier on doped Al(111), there is almost zero barrier for H₂ dissociation on Ti-doped Al(100). Specifically designed experiments are now required to determine if H₂ dissociation or surface diffusion is the rate-limiting step, i.e., which Al(hkl) surface allows more efficient alane formation.
- In situ FTIR spectroscopy revealed that Ti-doped Al(100) surfaces show higher concentrations of smaller alanes (AlH₃) than undoped surfaces. Higher Ti doping inhibits the formation of higher-mass alanes, likely due to stronger binding of the

FIGURE 2. FTIR spectroscopy showing different types of alane formation on (a) Ti-doped, (b) undoped Al(100) surfaces. (c) SEM image of Al(100) after several cycles of hydrogenation in H_2 , resulting in roughening but no alane formation.

Ti-doped surface and lower alane mobility, already found in our calculations (see above). SEM imaging reveals that Ti-doped Al(100) surfaces roughen dramatically upon repeated H_2 exposure, resulting in a substantial decrease of alane formation.

- The local bonding and atomic environments in the Ni-catalyzed destabilized system $LiBH_4/MgH_2$, and the quaternary borohydride-amide phase $Li_3BN_2H_8$ were studied by X-ray absorption spectroscopy [20]. A qualitative comparison of the Ni K -edge near-edge structure suggests that the Ni, introduced as Ni^{2+} , is reduced to primarily Ni^0 during ball milling. The extended fine structure of the Ni K -edge indicates that Ni is coordinated by about 3 boron atoms with an interatomic distance of ~ 2.1 Å, and about 11 Ni atoms in a split shell at around 2.5 Å and 2.8 Å. These results, and the lack of long-range order, suggest that the Ni catalyst is present as a disordered nanocluster with a local structure similar to Ni_3B . Calculations by density-functional theory suggest that the lowest kinetic barrier for H_2 chemisorption occurs on the $Ni_3B(100)$ surface.

2. Identification of the Carriers of Long-Range Mass Transport

- STM and IR spectroscopy on Al(111) in UHV, combined with DFT, have established how H atoms interact with the Al surface to form mobile alane species, and how these alanes interact, grow, diffuse, and desorb. Atomic-H first attaches at the step edge, leading to the formation of chemisorbed AlH_3 . At higher exposures, these alanes become physisorbed and agglomerate into larger alanes through oligomerization. STM shows a pronounced etching of Al surface steps during exposure to atomic H. Although difficult to interpret, IR spectra analyzed by comparison with DFT-predicted vibrational frequencies have unambiguously demonstrated the *formation of progressively larger alane species* with increasing H-coverage

and temperature, demonstrating the high surface mobility of these species [16].

- We have demonstrated the direct formation of alane from Al and H_2 at low pressure in the presence of a stabilizing molecule, such as an amine, to form an alane adduct. Raman spectroscopy and microscopy have been used to characterize various alane amines in the liquid and solid state.
- The assignment of alanes as a primary carrier of mass transport in the hydrogenation of alanates was confirmed by a series of targeted solid-state-chemistry experiments. Specifically, we were able to show that the hydrogenation proceeds readily *without the need for a catalyst* once alane is available [6]. This finding shows that alane formation is a critical step in the hydrogenation, and that this step is indeed enabled and accelerated by Ti doping.

3. Development of New Reversible Hydrogen Storage Materials

Experiments on bulk materials, accompanying our work on model systems in UHV, have focused on AlH_3 , a very promising H storage material with 10.1 wt% H-capacity. Little has been known about the crystallographic and thermodynamic properties of AlH_3 , and these have now been established:

- The thermodynamic and vibrational properties relevant for hydrogen storage of three different polymorphs, α , β , and γ - AlH_3 have been determined [8,15].
- High-pressure induced structural, chemical, and thermodynamic changes have been determined for α - AlH_3 , using combined high-pressure synchrotron X-ray diffraction and ab-initio calculations [7].
- The previously unknown crystal structures of β and γ - AlH_3 have been determined. For this purpose, a synthesis route for β - AlH_3 had to be established [10,14].

- The stability and decomposition pathways of the three AlH_3 polymorphs have been determined, showing an actual release of 10 wt% hydrogen at temperatures below 100°C. [11,12].

Our findings for both single crystal model systems and bulk materials suggest rational regeneration routes for AlH_3 and high-capacity alanates, by dissociating H_2 over Al doped with transition metals (Ti), generating molecular alane, which can then be collected and aggregated to a H-rich AlH_3 or alanate phase. Based on free energy arguments *regeneration in solution* holds the most promise. Fundamental research on the interaction of H with doped light metals (e.g., Al:Ti) in complex environments (e.g., liquids), necessary to establish the complex processes involved, have begun in FY 2008:

- We demonstrated a *low energy route to regenerate LiAlH_4* (10.6 wt% H) from LiH and Ti-catalyzed Al [17,19]. The initial hydrogenation in tetrahydrofuran (THF) forms the adduct $\text{LiAlH}_4\cdot 4\text{THF}$. The free energy change in this reversible reaction is small and slightly negative, suggesting an equilibrium H_2 pressure of ~1 bar at 300 K. The adduct $\text{LiAlH}_4\cdot 4\text{THF}$ was successfully desolvated at low T to yield crystalline LiAlH_4 . Regeneration of LiAlH_4 from LiH and Al hence is achieved in the two-step process:

The possibility of using this regeneration process for other metastable hydrides (e.g., $\text{Mg}(\text{AlH}_4)_2$) is currently being investigated.

Current Research and Future Plans

In ongoing and future work we aim to provide a comprehensive understanding of the role of dopants, nanoscale size effects, as well as complex reaction environments (e.g., fluids) in facilitating the hydrogenation and dehydrogenation of solid-state H-storage materials. A brief summary of these research directions is given below:

1. H_2 Dissociation at Surface Ti Complexes on Al Single Crystals

- Elevated-pressure STM is being used to establish how the hydrogen fuel to be stored (i.e., H_2) interacts with dopant sites on the surface of light metals, e.g., Ti on Al. Working closely with theory and IR spectroscopy important questions regarding the mechanism of H_2 dissociation and the formation of mobile molecular adsorbates (alanes) will be addressed.

- Impurities such as O_2 and H_2O , invariably present in practical storage materials, may fundamentally alter the interaction of hydrogen with light metals. UHV-STM and IR will be used to study their effects, in particular a possible enhancement or decrease in the activity of dopants.

2. Interaction of Hydrogen with Light Metal Nanoparticles

- Nanostructures could significantly enhance the kinetics of hydrogen storage reactions, but experiments at the atomic scale are needed to evaluate this possibility and identify the underlying mechanisms. We are preparing a study on the interaction of H with small metal and alloy nanoparticles in UHV, to understand the effects of nanoparticle size, of dopants at various concentrations, and of impurities, and to observe a possible dynamic reshaping of nanoparticles under H_2 or H exposure.

3. Surface Mass Transport and Initial Hydrogenation Stages

- Our previous work has shown complex H-metal interactions even for seemingly simple systems. A comprehensive model of the hydrogenation process will be invaluable to understand these interactions. By coupling DFT with KMC, we have begun to build a multiscale computational framework for different Al(hkl) surfaces. The energetics of atomic level processes, established by DFT, feed into KMC calculations on the evolution over large length and time scales. Once fully developed, this approach will serve to capture the complex processes involved in hydrogenation reactions and their modification by dopants.
- Experiments on surface mass transport during hydrogenation reactions will be carried out by STM and in situ low-energy electron microscopy. We will probe surface diffusion on Al and Ti doped Al surfaces, with and without H or H_2 exposure, as well as the initial nucleation and growth of hydrogen-rich phases on Al in the presence of NaH and H.

4. Mass Transport Through the Gas Phase

- Our experiments have shown that AlH_3 desorbs at about 370 K from Al surfaces (without Ti doping). Combined DFT and KMC calculations will be used to study temperature programmed desorption of different alane species on Ti-doped Al(khl) surfaces. As we have seen in the case of Al(100), larger alane species can be trapped at Ti sites, an effect that poisons the Ti sites and halts the further dissociation of H_2 . Desorption of these species may

help vacating the Ti sites, i.e., would reactivate the Ti catalyst for further H₂ dissociation.

5. Fundamental Mechanisms of Solution-Phase Hydrogenation of Al – Role of Dopants

- AlH₃ has recently been identified as a promising H-storage material with high storage capacity (>10 wt%) and fast dehydrogenation kinetics near ambient temperature. The key bottleneck to the widespread use of AlH₃, as well as of high-capacity complex hydrides that cannot be cycled reversibly in H₂ gas, is the lack of a viable regeneration route following its decomposition to H₂ and Al metal. Regeneration in solution appears promising. Yet it remains unknown how Al and doped Al interact with H₂ in a solvent such as THF. We are using powerful in situ spectroscopy experiments (Raman and infrared) in a microfluidic setup to study the reaction of H₂ on immersed Al (and Al-Ti) surfaces and the resulting formation of H-rich species (alanes and alane adducts) in solution. This work connects strongly with our studies on Ti-catalyzed model systems in UHV, and will establish hydrogen-metal interactions and their modification by dopants in complex environments, such as the liquid-solid interface.

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IV.I.10 Thermodynamics and Kinetics of Phase Transformations in Hydrogen Storage Materials

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- Obtained the activation energies for surface-controlled vacancy creation in pure undoped NaAlH_4 , showed that vacancy creation limits the dehydrogenation kinetics for particle sizes above $\sim 0.1 \mu\text{m}$.
- Identified a novel (γ) phase for NaAlH_4 , stable at room temperature, which is an intermediate transient in the dehydrogenation reaction.
- Studied H diffusion in the presence of NaH , AlH_3 , H^0 , and H^- vacancies in bulk NaAlH_4 , H^0 , and H^- interstitials in bulk NaAlH_4 , and an H^- vacancy in a (001) surface slab.
- Developed a first-principles theory of H diffusion in Al in the presence of defects.

Accomplishments

Reaction Kinetics and Dynamical Properties of Complex Hydrides

We have achieved significant progress in understanding fundamental atomic-scale mechanisms of phase transformations and mass transport in hydrogen storage materials. The activation energy for bulk Na diffusion via NaH vacancies is found to be significantly higher, $Q=112 \text{ kJ/mol H}_2$ (see Figure 1). Achievements are as follows:

- Showed that the calculated activation energy for AlH_3 vacancy diffusion in NaAlH_4 is 85 kJ/mol H_2 , suggesting that it is the rate-limiting step in hydrogen release kinetics from Ti-doped samples.

FIGURE 1. Proposed energy profile for the dehydrogenation pathway of NaAlH_4 via AlH_3 vacancies (blue curve). AlH_3 vacancies are created at the surface or at the Al/NaAlH_4 interface and diffuse towards $\text{NaAlH}_4/\text{Na}_3\text{AlH}_6$ interface, where they are annihilated by forming Na_3AlH_6 . The diffusion of NaH vacancies requires a higher activation barrier and is unfavorable. Dashed lines correspond to unknown energy barriers associated with the nucleation of product phases and interfacial reactions.

In sodium alanate, and most other modern hydrogen storage materials, H_2 release and uptake reactions are accompanied by long-range diffusion of metal species. Using density-functional theory (DFT) molecular dynamics simulations and the potential mean force umbrella sampling approach, we have previously obtained the activation energy for Al mass transport via neutral AlH_3 vacancies, $Q=85 \text{ kJ/mol H}_2$. This value is in excellent agreement with the experimentally measured activation energies in Ti-catalyzed NaAlH_4 of around 80 kJ/mol H_2 . *Our results suggest that bulk diffusion of Al species is the rate-limiting step in the dehydrogenation of Ti-doped samples of NaAlH_4 .* The calculated diffusion coefficient and vacancy concentration at typical decomposition temperatures ($D=4 \times 10^{-4} \text{ cm}^2/\text{s}$ and $\text{CV}=0.01\%$ at 400 K , respectively) are consistent with the observed dehydrogenation times of minutes to hours in ball-milled Ti-doped powders consisting of micron-sized grains. This study showed that Ti doping is not needed to obtain bulk mass transport at rates that are consistent with the observed dehydrogenation kinetics, and therefore the catalytic effect of Ti is not related to accelerated bulk diffusion. Since the measured activation energy in pure NaAlH_4 (118 kJ/mol H_2) is higher than our calculated activation energy for bulk diffusion of Al, hydrogen release from undoped NaAlH_4 is not limited by bulk diffusion, but could be controlled by surface or interfacial reactions. We have further refined our earlier calculations and investigated the possibility that the process of breaking an Al-H bond and creating a vacancy at the surface or at a multiphase interface (e.g., Al/NaAlH_4) is the rate-limiting step. The results of this study are shown in Figure 2. Using the generalized gradient approximation (GGA), we find that the generation of AlH_3 vacancies at the (001) surface requires an activation enthalpy of 96 kJ/mol H_2 . The competing

FIGURE 2. Zero-point energy corrected electronic energies and the structure of the transition state (marked by ‡) for creating charge-neutral AlH_3 and NaH vacancies at the (001) surface of sodium alanate. Al, H and Na atoms are shown as gray, white and purple spheres, respectively. Al atoms that are changing their bonding environments during the reactions are colored green, and H atoms that are attached to these Al atoms are colored black. The surface Na^+ ion obtained upon forming the NaH vacancy is blue.

diffusion pathway via the creation of NaH vacancies was found to require 130 kJ/mol H_2 at the (001) surface, significantly higher than that required for the AlH_3 vacancy process. More accurate quantum chemistry calculations at the CBS-QB3 level for the activation enthalpy of breaking the Al-H bond, $\text{AlH}_4^- \rightarrow \text{AlH}_3 + \text{H}^-$, show that the DFT tends to underestimate the Al-H bond enthalpies by 24 kJ/(mol H_2). The corrected activation barrier, 120 kJ/mol H_2 , is higher than the computed bulk diffusion barrier (85 kJ/mol H_2), and agrees very well with the experimental data for undoped NaAlH_4 , indicating that vacancy creation is indeed be the rate-limiting step in pure NaAlH_4 . We have computed the critical particle size where crossover from bulk-diffusion dominated kinetics to surface vacancy-creation dominated kinetics occurs. We find that *for particle sizes on the order of 0.1 μm and above, the surface vacancy creation is the rate-limiting process for dehydrogenation, and therefore one of the catalytic functions of Ti is to facilitate the breaking of Al-H bond*

We have also been performing extensive studies of the dehydrogenation of NaAlH_4 using total energy and total free energy calculations, linear-response theory, and first-principles molecular dynamics. We take this material as a paradigmatic example for what insight simulations can give on the thermodynamics and kinetics of the reaction – in addition, despite a wealth of recent, the precise mechanism of dehydrogenation, as well as the role of the dopants (e.g. titanium) in enhancing the reaction chemistry, remains unknown. Moreover, given the complexity of the configurational phase space and the difficulty of isolating dominant reaction pathways, it is unlikely that static energetic calculations will ever be fully capable of capturing

the reaction kinetics. We have focused on the first dehydrogenation reaction ($\text{NaAlH}_4 \rightarrow 1/3 \text{Na}_3\text{AlH}_6 + 2/3 \text{Al} + \text{H}_2$), which is thought to be more useful under actual operating conditions. The key result is our *discovery of a novel phase, thermodynamically more stable than the reactant alanate at temperatures greater than 250 K, that bears a striking topological similarity with the end product Na_3AlH_6 , and whose vibrational signatures are in agreement with recent experimental observations.*

In Figure 3, we present the structure of this new phase of NaAlH_4 , which we will designate as γ . When relaxed with respect to all internal parameters and lattice vectors, the unit cell is best described as a 12-atom base-centred orthorhombic structure, with $a = 6.652 \text{ \AA}$, $b = 7.235 \text{ \AA}$, and $c = 7.243 \text{ \AA}$. We compared the total energy of this new structure, calculated using 216 $\mathbf{k}$ -points, to that of the ground-state α phase, calculated using a 324- $\mathbf{k}$ point mesh of similar density. At 0 K, the α phase is more stable energetically by only 8 meV/atom, pointing to a close competition for stability between these two phases. In order to establish finite-temperature properties, we have calculated the phonon dispersions for the α and γ phases using density-functional perturbation theory. shows the results of this calculation along high-symmetry directions in the orthorhombic unit cell of $\gamma\text{-NaAlH}_4$ (results for $\alpha\text{-NaAlH}_4$ are not explicitly shown but are in close agreement with published results). Phonon bands below 180 cm^{-1} represent the Na/Al translational lattice modes; bands in the 180–400 cm^{-1} range represent the AlH_4 rotational modes; and bands in the 750–900 cm^{-1} range represent the Al-H bending modes. High-frequency Al-H stretching modes (1,650–1,820 cm^{-1}) are not depicted. Figure 4(c) points to the essential qualitative difference between the phonon dispersions of the two phases: the bands corresponding to the AlH_4 rotational

FIGURE 3. Structure of orthorhombic $\gamma\text{-NaAlH}_4$ shown (a) in the standard view; (b) along a , and (c) along c . Na atoms are shown in blue, Al in green, and H in white.

FIGURE 4. Phonon spectrum of γ -NaAlH₄ along the high-symmetry directions depicted in (a). Frequencies above 900 cm⁻¹ are not shown. The solid arrow indicates the highest frequency of occupied bands at the $\alpha \rightarrow \gamma$ transition temperature. Inset (b) shows the temperature-dependent free-energy difference between the two phases. Panel (c) compares the phonon densities of states for the γ phase (solid line) and the α phase (shaded region).

modes, which fall in the 350–550 cm⁻¹ range for the α phase, are substantially softened in the γ phase. This softening results in an increase in vibrational entropy at temperatures for which these modes are active. We estimate the temperature-dependent free energy $F(T)$ of the two phases by adding the Bose-Einstein vibrational entropy contribution onto the ground-state total energy. Neglecting further contributions to $F(T)$, we find a thermodynamic preference for the γ phase over the α phase for temperatures above 252 K (see Figure 4(b)). Notably, this establishes the γ phase as the most stable variant within the experimental temperature range for dehydrogenation. In a recent in situ Raman study, Yukawa et al. (J. Alloys Comp. 446-447, 242 (2007)) found evidence of an unknown intermediate phase in first-stage dehydrogenation. The authors suggest that, like our proposed γ phase, this new phase is stable at room temperature and contains intact AlH₄ units with little constraint from the crystal lattice. Accompanying this intermediate, they record the emergence of a new signature vibrational peak for Al–H stretching near 1,800 cm⁻¹. While absent for α NaAlH₄, this peak is clearly manifest in our calculated phonon density of states for γ , making the latter a likely candidate for the unidentified phase.

Hydrogen Kinetics in Aluminum

Measuring the diffusion rate of hydrogen in metals is important for understanding the kinetics of hydrogen storage, hydrogen-induced deterioration in the

mechanical properties (e.g. embrittlement and cracking) and electrochemical charging of metals. However, a consensus on the physical mechanisms and numerical values of H diffusion coefficients in metals is still lacking. Even in the widely studied case of H in Al, published experimental measurements of the activation enthalpy and pre-exponential factor range from 0.17 to 0.94 eV and from 10⁻¹ to 10⁻⁴ cm²/s, respectively. Disparity in the measured rates is often attributed to the difficulties in measuring H diffusion accurately due to low solubility of H in Al and due to binding of H to structural defects. Based on the results of earlier first-principles calculations, we have developed a quantitative theory of hydrogen diffusion in aluminum with lattice defects. *Ab initio* molecular dynamics simulations have been used to obtain the activation energy and prefactor for lattice diffusion of H in Al between 650 and 850 K: $\Delta H^\ddagger = 0.12 \pm 0.02$ eV and $D_0 = 1.1 \times 10^{-7}$ m²/s. Vacancies are found to significantly decrease the apparent diffusivity due to their ability to bind hydrogen atoms, causing a strong composition-dependence and non-Arrhenius behavior of the effective diffusion coefficient. The effective experimentally measured diffusion coefficient is given by the following expression:

$$D = D_L / \left(1 + \frac{\partial C_{\text{trap}}}{\partial C_L} \right)$$

which depends on the hydrogen concentration in the lattice (C_L) and trap (C_{trap}) sites. Hydrogen exchange between the lattice and vacancies leads to an apparent reduction in the diffusion coefficient, explaining the wide disparities in the measured activation energies and prefactors (see Figure 5). Finally, we show that an earlier suggestion by Lu and Kaxiras [Phys. Rev. Lett. **94**, 155501 (2005)] that up to twelve hydrogen atoms may get trapped in one vacancy, is not expected to occur

FIGURE 5. Calculated correction factor to the apparent diffusion coefficient, $(1 + \partial C_{\text{trap}} / \partial C_L)^{-1}$ as a function T and C_H .

at reasonable temperatures and hydrogen pressures (Figure 6).

Nano-Scale Effects on the Thermodynamics and Structure of Hydrogen Storage Materials

In previous years we focused on predicting the structure and thermodynamics of hydrogen storage materials. This year we initiated our study of the size effects on the structure and thermodynamics of hydrogen storage materials. Dealing with nanomaterials is considerably more complex than with bulk materials as there are no periodic boundary conditions and the role of the surfaces is crucial. Towards the objective of understanding nanomaterials we achieved the following results:

- Developed novel cluster expansion techniques to predict atomic ordering and structure of nanoparticles.
- Applied the new approach to sodium alanate (NaAlH_4) to predict the shape of small nanoparticles of this material.

Sodium alanate is a widely-studied hydrogen storage material, with a theoretical gravimetric capacity of 5.6%. Bulk sodium alanate releases hydrogen at temperatures well above 100°C, which is too high for use in PEM fuel cells. However it has recently been shown that 2-10 nm sodium alanate nanoparticles release hydrogen at a peak temperature of 70°C, which is within the target range for PEM fuel cells. The activation energy for hydrogen release in nanoparticles is significantly lower than the bulk activation energy for reasons that remain unknown.

FIGURE 6. Left: average number of H atoms per vacancy, n_v , as function of the total hydrogen concentration. Red, blue and green curves represent $T=363$, 600, and 800 K, respectively.

The morphology of NaAlH_4 nanoparticles may play a significant role in lowering the activation energy for hydrogen release, but determining the shape of nanoparticles is both experimentally and computationally challenging. A common method for determining equilibrium particle shape is the Wulff construction, in which the distance between the center of the particle and a (lmn) surface facet is proportional to the bulk (lmn) surface energy. However, because the Wulff construction assumes large surfaces and ignores edges, vertices, and size effects, it is better suited for large particles than 2-10 nm nanoparticles. In addition, the Wulff construction requires that the complete set of relevant surfaces is already known. As an alternative to the Wulff construction, we have developed a cluster expansion. Hamiltonian trained on density functional theory calculations that enables us to rapidly and accurately calculate the energy of a particle with a given shape. Using the cluster expansion, we are able to predict the shape of NaAlH_4 nanoparticles by directly searching for the shape with the lowest energy. This approach naturally incorporates edge and vertex effects and allows the determination of particle shapes without *a-priori* knowledge of the important surfaces. In Figure 7, we show the difference between the shape predicted by a Wulff construction and the shape predicted by the cluster expansion for a sodium alanate nanoparticle that is about 6 nanometers wide.

The cluster expansion approach reveals new surfaces and sites that may be keys to understanding the enhanced activity of NaAlH_4 nanoparticles. For example, the (116) surface of sodium alanate is not close-packed and was not considered as a potential low-energy surface in previous studies [6,7]. However nanoparticle shapes predicted by the cluster expansion have notable (116) facets. Based on the insights from the cluster expansion, we have used density functional theory to calculate the (116) surface energy. Our calculations indicate that the (116) surface is one of the lowest-energy surfaces for sodium alanate, suggesting that it may play an important role in hydrogen storage and release reactions.

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FIGURE 7. The predicted ground state shape of a NaAlH_4 nanoparticle predicted by (a) a Wulff construction, and (b) the cluster expansion method. Orange spheres represent Na, and blue sphere represent AlH_4 groups.

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IV.I.11 Control of Hydrogen Release and Uptake in Condensed Phases

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- LANSCE: Luke Daemen, Hyunjeong Kim, Thomas Proffen

Contract Number: DE-AC05-76RL01830

Motivation

Energy from renewable resources (e.g., solar and wind) are critical to a clean energy future. Methods to store renewable energy (e.g., hydrogen) are required to balance energy production with energy demand. The long-term objective of our research is to gain fundamental insight into the chemical and physical properties of hydrogen-rich materials that will provide the basis for developing new hydrogen storage systems.

Outstanding Issues

- Molecular level interactions play an important role in the kinetics and thermodynamics of hydrogen release and uptake in condensed phases.
- How do dihydrogen bonding interactions affect the structure and dynamics of hydrogen rich molecular crystals (ammonia borane, ammonium borohydride, amido boranes)?
- What are the inherent structures of catalysts that facilitate the release of hydrogen from these inorganic materials containing both hydridic and protonic hydrogen?
- How do environmental factors such as nano-confinement modify the thermodynamics and kinetics of molecular crystals?

Approach

Use experiment and theory to gain insight into mechanisms of environmental conditions, (i.e., electrostatic interactions, nano-confinement, catalysis), that provide tunable parameters to enhance kinetics and modify the thermodynamics in hydrogen-rich molecular crystals.

One critical aspect of hydrogen storage is the kinetics of hydrogen release and uptake from

materials containing ionic or covalently bound hydrogen. Specifically we are studying how the reaction environment can be used to control reactivity and selectivity of a reaction pathway. Fundamental insight into mechanisms of external parameters such as catalysis, nano-confinement, and electrostatic molecular interactions can all provide tunable mechanisms to enhance the kinetics of hydrogen release and uptake. Of special interest is the dynamics of dihydrogen bonding, the interaction between hydridic and protonic hydrogen. These electrostatic interactions between molecules affect both the structure and dynamics of hydrogen rich materials in the condensed phase. We have proposed that materials composed of both hydridic and protonic hydrogen will lead to enhanced kinetics for hydrogen release. To gain some fundamental insight into this hypothesis our group uses spectroscopic methods (NMR, Raman and Neutrons) to study the dynamics of hydrogen bonding interactions in condensed phase materials. We are also interested in catalysts that activate the release of hydrogen from materials containing both hydridic and protonic hydrogen and use in situ XAFS to directly study sub-nano metal clusters that active the release of hydrogen bonded to light elements.

At present we are studying the structure and dynamics of ammonia borane NH_3BH_3 . This compound, a simple donor-acceptor complex formed by a dative bond between the non-bonding electrons on nitrogen with the empty p-orbital of borane, organizes in to a molecular crystal by virtue of (1) dipole-dipole interactions and (2) the di-hydrogen bonds formed between the protonic NH and hydridic BH groups in adjacent molecules. We believe the interactions between the hydridic and protonic hydrogen

FIGURE 1. Orthorhombic phase (N = violet, B is turquoise, H = white) showing di-hydrogen bonding network in molecular crystal of ammonia borane.

leads to the low temperature loss of hydrogen in solid state ammonia borane.

Our group has experience in synthetic chemistry that enables us to make selectively labeled materials for spectroscopic investigations. Preparation of ^{11}B enriched boron compounds enhances results from our neutron scattering work. For NMR studies we prepare ^{15}N enriched materials for in situ kinetic studies. Alternatively we can selectively incorporate deuterium into the molecule to mask the neutron signal or emphasize the NMR signal. (NH_3BH_3 , $^{15}\text{NH}_3\text{BH}_3$, $^{11}\text{BH}_3\text{NH}_3$ and the corresponding deuterium labeled compounds ND_3BH_3 , ND_3BD_3 , NH_3BD_3 .)

a. Neutron Scattering Spectroscopy (in collaboration with Luke Daemen and Thomas Proffen at LANSCE)

Neutron scattering methods are ideally suited for investigation of light elements and in particular hydrogen. A variety of neutron scattering methods are well suited to study the structure and dynamics of

molecular crystalline ammonia borane. Neutron powder diffraction (NPDF) can be used to obtain structure as a function of environment (temperature, pressure, nano confinement) and to yield specific location of hydrogen atoms. Inelastic incoherent neutron scattering (IINS) provides low temperature vibrational spectra to study chemical bonding and dynamics, including hydrogen bond dynamics. The spectrum is also a useful fingerprint to identify ammonia-borane and the effect on the solid of chemical environment.

Neutron Powder Diffraction (NPDF). Diffraction patterns at different temperatures, above and below the 220 K phase transition have been collected on the Neutron Powder Diffractometer, NPDF – a high-resolution total scattering powder diffractometer at LANSCE. At 175 K, the axes of ammonia-borane molecules are nearly aligned with the c-axis of the unit cell and the adjacent $-\text{BH}_3$ and $-\text{NH}_3$ groups are not quite coplanar. There are 6 total hydrogen bonding interactions per molecule providing a calculated cohesive energy of 76-90 kJ/mol, however, the rotational barrier of the $-\text{BH}_3$ and $-\text{NH}_3$ groups are surprisingly low indicative of very dynamic motion.

Incoherent Inelastic Neutron Scattering. (IINS). We used the filter difference spectrometer (FDS) at LANSCE to collect low frequency vibrational spectra of three ammonia-borane isotopomers: $\text{NH}_3^{11}\text{BH}_3$, $\text{ND}_3^{11}\text{BH}_3$, and $\text{NH}_3^{11}\text{BD}_3$. Isotopic substitution takes advantage of the large incoherent scattering cross section

FIGURE 2. Experimentally measured thermal ellipsoids from neutron diffraction experiments at temperatures above and below the phase transition. The size of the ellipsoids about the B and N atoms suggests the hydrogen is substantially more mobile in low temperature phase (top) than room temperature phase (bottom).

FIGURE 3. Calculated thermal ellipsoids for the same structures. There are weaker interactions between the hydrogens in the room temperature phase of AB is likely the discrepancy for the structure and dynamics.

FIGURE 4. Comparison of the low frequency (cm^{-1}) torsional modes in the vibrational spectrum of ammonia-borane, $\text{NH}_3^{11}\text{BH}_3$ obtained from experimental and MD simulation (CP2K dynamics). The blue line is experimental (IINS) and the red line is the simulated spectra focused on the NH_3 side of the molecule and the black line is the simulated spectra focused on the BH_3 side of the molecule.

of hydrogen (compared to deuterium) to facilitate vibrational mode assignment. The low frequency portion of the vibrational spectrum of ammonia-borane is shown in Figure 4. The relatively broad band at 350 cm^{-1} is the torsional mode of the molecule in which NH_3 and BH_3 rotate about the B-N axis with opposite phases. This mode is not IR- or Raman-active. The 350 cm^{-1} band in the experimental vibrational spectrum is somewhat broader than the internal modes and much broader than the external modes below 250 cm^{-1} . Preliminary MaxEnt analysis suggests that this band maybe comprises two bands at slightly different frequencies. Computational work is in progress to develop models to help understand the fundamental properties of hydrogen bonding interactions in ammonia borane.

b. NMR Spectroscopy

We are using $2\text{H } ^2\text{H}$ NMR to probe the rotational dynamics in solid phase ammonia borane (NH_3BH_3). Both the ^2H line-shape and ^2H spin-lattice relaxation rate (T_1^{-1}) exhibited strong anomalies around 220 K . The analysis of T_1^{-1} using the Bloembergen-Purcell and Pound (BPP) model showed that the motional correlation time, τ , increased from about 1 ps to 100 ps while the corresponding Arrhenius activation energy increased from 6 to 13.4 kJ/mol for the NH_3 rotor motion. $^2\text{H } T_1^{-1}$ measurements were obtained for $-\text{ND}_3$ and $-\text{BD}_3$ rotor motion over the temperature range from 220 K to 80 K . At higher temperatures ($>100\text{ K}$) the rotational barrier for $-\text{ND}_3$ (13.7 kJ/mol) was consistent with the barrier $-\text{NH}_3$ rotation, however at lower temperatures there appears to be an anomaly in the experimental observations. A change in the rotational dynamics could be due to the change in structure as observed by NPDE.

Preliminary calculations (on a cluster of 8 ammonia boranes) performed for the 175 K structure at the DFT level of theory shows great correlation with the rotational barriers determined by NMR T_1^{-1} experiments.

c. XAFS Spectroscopy (APS)

We have been interested in developing an understanding of catalytic activation of hydrogen release from amine boranes using a combination of *operando* XAFS and NMR techniques. Operando spectroscopy permits the direct observation of key intermediates under reacting conditions, i.e., at reaction pressure and temperature, to gain insight into catalytic processes. Operando X-ray absorption fine structure (XAFS) spectroscopy has enabled us to identify and characterize a four Rh atom cluster that is a critical species involved in the catalytically-induced release of H_2 from amine

FIGURE 5. DFT calculated barrier for rotation of -NH_3 (pathway II, 13.1 kJ/mol), -BH_3 (pathway IV, 30.7 kJ/mol) and whole molecule rotation NH_3BH_3 (pathway III, 22.4 kJ/mol) at 175 K. Our calculations confirm the higher rotational barrier for BH_3 compared to NH_3 as observed by experiment (^2H NMR T_1^{-1} and QENS). The ground state structure is stabilized by di-hydrogen bonding, however there is greater repulsion between the H-atoms in BH_3 rotational plane.

boranes. These results demonstrate that metallic nanoparticles are not directly involved in the catalyzed release of H_2 . These are important findings that will enable the design of concepts to control transformations in a multitude of related catalytic processes. XAFS spectroscopy shows that the predominate rhodium species formed under the catalysis conditions is a Rh_4 cluster (diameter of approximately 0.3 nm) rather than a 2 nm-diameter Rh nanoparticle. Knowledge of the Rh structures provides key insights into the catalysis species and the mechanism of the formation of hydrogen from amine borane compounds.

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FIGURE 6. Comparison of simulated and experimental XAFS spectra of rhodium species formed from the catalyst precursor Rh(cod)chloride and dimethylamine borane. Structure on the bottom is obtained by molecular dynamics simulations and shows the potential resting state of the active Rh(4) cluster. Each Rh atom has two boron ligands.

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IV.I.12 First Principles Based Simulation of Hydrogen Interactions in Complex Hydrides

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Summary of Accomplishments

Our overall goal is to develop a multiscale approach to model desorption and adsorption of hydrogen in complex metal hydrides. We predicted the TiAl_3H_x complex as the precursor for forming TiAl_3 alloy observed in Ti-doped NaAlH_4 . We then showed that doped 3d transition metals form similar interstitial structures, and examined the effect of doped transition metals on reversible hydrogen release/uptake from NaAlH_4 . We also explored effect of hydrogen spillover in rehydriding Li_3N in collaboration with an experimental group.

(a) Effect of Doped Transition Metal on Reversible Hydrogen Release/Uptake from NaAlH_4

Periodic density function theory calculations with plane-wave basis set and projector-augmented wave potentials have been carried out to investigate the stability and hydrogen interaction in the $\text{NaAlH}_4(001)$ surfaces doped with 3d transition metal (TM) elements. A complex structure, $\text{TMAI}_3\text{H}_{12}$, in which the TM atom occupies the interstitial position formed from three AlH_4^- groups, is the most stable structure for $\text{TM} = \text{Sc}$ to Co . The stability of the complex structure, as well as the hydrogen desorption energies from different positions of the complex structure, was found to follow the 18-electron rule in general. The hydrogen desorption process has been considered as a stepwise process: the H atoms first recombine (R) on the TM site to form dihydrogen as an intermediate and the intermediate is then separated (S) from the TM site. These steps as well as the associated energy costs for each TM were plotted in Figure 1. The electron-deficient TMAI_3H_x tends to get more electrons by coordinating with the surrounding Al–H bonds and H–H bond, or by losing the “outside” hydrogen atoms. On the other hand, the electron-rich complex loses its excess electrons easily by releasing AlH_x , which resulted in the formation of

FIGURE 1. Variation of recombination, separation, and desorption energy of $\text{H}_7\text{-H}_8$ in $\text{TMAI}_3\text{H}_{12}$ with TM.

a new catalytic center, or by desorbing H_2 . By cycling between the electron-deficient and electron-rich states, TMAI_3H_x acted as an active center in the reversible hydrogen release/uptake processes. Electronic structure analysis revealed that the electron transfer between hydrogen and Al groups mediated by the d-orbitals of TMs played important roles in hydrogen release/uptake from alanate-based materials. As shown in scheme 1, the exchange of ligands can be described as a σ -bond metathesis process catalyzed by TM through a dihydrogen complex. Early TMs are more efficient to reduce hydrogen desorption energy and break H–H and Al–H bonds as a result of balanced electron accepting/backdonating abilities, making them better candidates as catalysts. The present analyses are consistent with the experimental observations. (*Chemistry – A European Journal*, 15, 1685 (2009))

SCHEME 1. The two-step σ -bond metathesis process with four-membered intermediate ($\text{TM-Al}_2\text{-H}_7\text{-H}_8$).

(b) Ti-Doped $\text{LiBH}_4(001)$, (100), and (010) Surfaces

Density function theory studies have been carried out to investigate the energetics and structures of Ti-doped $\text{LiBH}_4(001)$, (100), and (010) surfaces. We

examined possibilities of Ti occupying various positions at these surfaces, including substitution, surface adsorption, and interstitial insertion. Among all possible structures, a Ti atom prefers energetically to occupy the interstitial positions consisting of three or four BH_4^- hydrides. The most stable species in the three surfaces have a similar local structure, as shown in Figure 2, and can be described as $\text{TiB}_2\text{H}_8\text{-nBH}_4$ ($n=1,2$). Furthermore, these complex structures and their transformation are localized. Molecular orbital analysis of the local structure showed that the structural stability can be attributed to the symmetry-adapted orbital overlap between Ti and “inside” hydrogen atoms. The hydrogen desorption energies from many positions of these local complex structures were found to decrease significantly with respect to that from the clean surface, which is consistent with the experimental observations. The most favorable hydrogen desorption pathways led to the formation of the dehydrogenation product in a triplet state. Consequently, the triplet $\text{TiB}_2\text{H}_8\text{-BH}_4$ in (001) and $\text{TiB}_2\text{H}_8\text{-2BH}_4$ in (010) will desorb a hydrogen molecule, while the quintet $\text{TiB}_2\text{H}_8\text{-BH}_4$ in (100) will desorb atomic hydrogen. Detailed electronic structure analysis revealed that the electron backdonation from the d orbitals of Ti to the antibonding orbitals of BH_4^- in $\text{TiB}_2\text{H}_8\text{-nBH}_4$ ($n=1,2$) is not as significant as those to the antibonding orbitals of AlH_4^- in $\text{TiAl}_3\text{H}_{12}$. Consequently, the B–H bonds in $\text{TiB}_2\text{H}_8\text{-nBH}_4$ ($n=1,2$) were not as highly activated as the Al–H bonds in $\text{TiAl}_3\text{H}_{12}$. (submitted)

(c) Hydrogen Spillover Enhanced Hydriding Kinetics of Palladium-Doped Lithium Nitride

Hydrogen storage in complex metal hydrides often suffers from unsatisfied hydriding kinetics of the corresponding complex metals under moderated conditions, partly due to the kinetic barrier associated with the breaking of H–H bond. Therefore, doping catalysts for H–H bond breakage becomes a feasible strategy to improve the hydriding kinetics because hydrogen adatoms can efficiently spillover from catalyst to complex metals. To implement this strategy, Dr. Tao Xu of Northern Illinois University, our experimental collaborator, developed a unique method to uniformly dope catalytic metal in the storage complex via synthesis of the eutectic of the catalytic metal and the precursory storage material. This method eliminates the use of support materials for catalysts, while still maintains the

FIGURE 2. The DFT-GGA relaxed structures of Ti doped LiBH_4 surfaces.

large surface area and uniformity of the catalysts. Our results demonstrated that $\text{Li}_3\text{NPd}_{0.03}$ with nanoscopic Pd uniformity can be prepared through nitridization of $\text{LiPd}_{0.01}$ eutectic. The synthesized $\text{Li}_3\text{NPd}_{0.03}$ exhibits an enhanced hydriding kinetics over pure Li_3N for reaction $\text{Li}_3\text{N} + \text{H}_2 \leftrightarrow \text{Li}_2\text{NH} + \text{LiH}$ under moderate conditions. The experimental measured an activation barrier of ~ 28 kJ/mol for hydriding $\text{Li}_3\text{NPd}_{0.03}$. We used a Pd_4 cluster supported on the (100) surface of Li_3N to analyze the hydrogen adsorption and migration processes and determined the diffusion barrier using the DFT calculations. We focused on the migration of the hydrogen adatom from the supported Pd_4 to the neighboring N site. Figure 3 shows a potential energy profile for a hydrogen adatom to diffuse from the bridge-bound configuration on the supported Pd_4 cluster (A) to the N atom in the Li_3N slab (C). As shown in the figure, the overall diffusion process for H from adsorbed on the Pd_4 cluster to bond to N is energetically favorable, manifested by an energy gain of 0.684 eV. This diffusion process is activated, with a diffusion barrier calculated to be 0.257 eV, i.e. ~ 25 kJ/mol. This result is in good agreement with the value from analysis of the experimental kinetic data and indicates that the hydriding kinetics is limited by H adatom diffusion. (*Journal Physical Chemistry C*, ASAP)

(d) Phase Transition of NaAlH_4 Followed by Metadynamics

Experimental studies have established that hydrogen release from NaAlH_4 -based material is accompanied by a series of phase transitions in solid

FIGURE 3. Potential energy profile of H adatom diffusion from Pd to N.

state. The process starts with NaAlH_4 , goes through a Na_3AlH_6 intermediates and finishes with NaH and Al . Traditionally, constant-pressure molecular dynamics can be used to follow the structural transformation in this process. However, the complex potential energy landscape and nature of the system made the traditional MD ineffective. Metadynamics allows the system to escape from free-energy minima and provides a more effective sampling of the potential energy surface. In our simulation, we treated the simulation box edges $h=(a, b, c)$ as a collective coordinate to explore the structural transformation. These parameters evolve according to the combined driving force derived from stress and a history-dependent Gaussian function. In between the meta steps, the system was allowed to equilibrate by following the regular molecular dynamics trajectory at constant T and P . During a metadynamics run, we monitor the change in pairwise distances and use these distances as a measure of formation of certain species.

We run a number of test metadynamics simulations at different temperatures (400, 600, 800 K) with a fixed pressure (100 bar). Figure 4 plots the probabilities of various species formed as system evolves with the metadynamics steps. As shown in Figure 4, more NaH , AlH_6 and AlH_5 species are formed with the increased simulation temperatures. The formation of NaH causes AlH_4 to lose its electron and promote polymerization of

hydrides through a μ -hydrido-bridge bond. The mobile H^- may react with the hydrogen atom of electron-deficient polymer, thereby form a hydrogen molecule. This late step remains to be seen in the simulation. (To be published)

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3. Jiamei Yu, Jianjun Liu, & Qingfeng Ge, " TiAl_3 : Structure and its interaction with hydrogen", 2008 CCC Spring Symposium, Lisle, IL, May 15, 2008 (poster).

FIGURE 4. Probabilities of NaH and AlH_n ($n=3$ to 5) formation followed by metadynamics.

4. J. Yu, J. Liu, & Q. Ge, "TiAl₃: Structure and its interaction with hydrogen", 235th ACS National Meeting, New Orleans, April, 2008 (poster).
5. N. Sullivan, J. Liu, & Q. Ge, "Dissociation and isomerization of B₂H_x on Pt (111)", 235th ACS National Meeting, New Orleans, April, 2008 (poster).
6. J. Liu, Y. Han & Q. Ge, "Comparison on hydrogen desorption mechanisms for Ti-doped NaAlH₄ and LiBH₄ surfaces", 39th Midwest Theoretical Chemistry Conference, Bloomington, IN, June 28–30, 2007 (poster).
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9. J. Yu, J. Liu & Q. Ge, "A first principles study of TiAl₃ clusters and its effect on hydrogen storage", 39th Midwest Theoretical Chemistry Conference, Bloomington, IN, June 28–30, 2007 (poster).
10. L. Cheng, J. Liu & Q. Ge, "Hydrogen Adsorption and Dissociation over Mg Clusters", 39th Midwest Theoretical Chemistry Conference, Bloomington, IN, June 28–30, 2007 (poster).
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19. J. Liu & Q. Ge, "First-principle study on Ti interaction with NaAlH₄ (001) Surface", 231st ACS National meeting, Atlanta, GA, Mar. 26–30, 2006 (poster).
20. Q. Ge, "A first principles analysis of the surface structure and energetics of complex metal hydrides", Gordon Research Conference on Hydrogen-Metal systems, Waterville, ME, July 10–15, 2005 (poster).

Seminars

1. Department of Chemistry, University of Missouri, Columbia, Oct. 14, 2008.
2. Institute for Fuel Cell Innovation (IFCI), National Research Council Canada (NRC), Vancouver, Canada, July 15, 2008.
3. Pacific Northwest National Laboratory, July 10, 2008.
4. Department of Chemistry & Biochemistry, Northern Illinois University, Feb. 11, 2008.
5. SINOPEC Tianjin University R&D Center for Petrochemical Technology, Tianjin University, Jan. 11, 2008.
6. Department of Chemistry, TsingHua University, Jan. 3, 2008.
7. Institute of New Energy Material Chemistry, Nankai University, June 22, 2007.
8. School of Chemical Engineering and Technology, Tianjin University, June 14, 2007.
9. Department of Chemical Engineering, University of Illinois at Chicago, Mar. 9, 2006.

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IV.I.13 NMR of Hydrogen Storage Systems: Ionic Hydrides and Mobile Species

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Major Accomplishments for Period 01 September 2008 – 15 April 2009

In the past, hydrogen storage solids were almost exclusively *interstitial metallic hydrides*. These are noted for their generally good hydrogen diffusion kinetics; here we report ω_H , the rate of atomic-level hydrogen hopping events. This is nicely demonstrated in Figure 1, where ω_H appears on a logarithmic scale for the prototypical ionic system MgH_2 and in the metallic systems ScH_2 , Mg-ScH_x , and $\text{LaNi}_5\text{H}_{6.8}$. Clearly, MgH_2 has much slower dynamics than the metals, and a much higher activation energy. Remarkably, MgH_2 can be converted from the rutile (ionic) structure to the fluorite (metallic) structure with as little as 20% Sc, though Figure 1 is for 35% Sc; the H hopping in the metallic phase is much faster than in MgH_2 and is even a bit faster than in ScH_2 .

FIGURE 1.

While the metallic hydrides show good H kinetics, an essential feature of any hydrogen storage system, the mass-fraction of H, is too small. Thus, interest has turned to the lightweight hydrides, such as LiH , MgH_2 (7.6 w/w%), NaMgH_3 , and LiBH_4 (18 w/w%). These are all *ionic* or *complex* hydrides. We examined coarse-grained MgH_2 as the prototypical ionic hydride. The rate ω_H of H hopping remains too slow to narrow the hydrogen NMR line up to 400°C , so $\omega_H < 10^5 \text{ s}^{-1}$. This confirms the reputation of MgH_2 for slow kinetics – rehydriding Mg metal often is halted once a thin skin of MgH_2 forms and blocks further reaction progress.

To detect and measure such slow motions, we turned to the ultraslow motion experiment of Ailion and Slichter. Standard spin Zeeman-order is converted to spin dipolar-order at the start of the experiment. This order is found to decay with time constant T_{1D} . Because dipolar order is a correlation between a spin's orientation and the local dipolar field from its neighbors, and because the local field varies from site-to-site with little correlation, a single atomic jump destroys a given spin's contribution to the dipolar order. Thus, the measured relaxation rate $1/T_{1D}$ is essentially equal to the rate of atomic jumps for a typical H atom.

Results are presented in Figure 2 for coarse-grain MgH_2 . The straight-line region represents thermally activated H motion, from 0.1 s^{-1} at 250°C to 400 s^{-1} at 400°C ; these are indeed slow motions. The activation energy is 1.72 eV ($\pm 7\%$), a high value that explains the slow kinetics of MgH_2 . At lower temperatures, the data curve and are no longer controlled by H kinetics; the

FIGURE 2.

dipolar order decays through coupling to the ^{25}Mg spins and the quadrupolar T_1^{-1} process. The overall fit to the data incorporates both mechanisms and is excellent.

We investigated a number of ball-milled MgH_2 materials supplied by collaborators at Savannah River, Université de Québec Trois Rivières, and GKSS (Germany). Lineshape data are presented in Figure 3a for the most “accelerated” system – MgH_2 with 0.5 mol% Nb_2O_5 from GKSS. Already at 100°C , a line-narrowed component appears, indicating a small fraction of mobile H atoms (here “mobile” means $\omega_H > 10^5 \text{ s}^{-1}$). With increasing temperatures, the fraction of intensity in the narrowed line (see graph in Figure 3b) increases up to ~31% at 400°C . Two aspects are worthy of note: mobile H atoms appear already at low temperature (100°C) and the sample is *inhomogeneous*, with some slow-moving H and some fast moving. Presumably, the sample inhomogeneity reflects a very broad distribution of local environments, due to the aggressive mechanical activation process.

FIGURE 3.

In addition, the relaxation time T_1 decreases from 3,000 s to 0.1 s in the ball-milled GKSS material. This rapid relaxation, only weakly temperature dependent, demonstrates a large concentration of unpaired electron spins from mechanical rupture of the bonds.

The behavior of ball-milled MgH_2 is similar to NaMgH_3 , ball-milled from 1:1 NaH and MgH_2 . The hydrogen NMR line narrows starting below 100°C . The narrowing is inhomogeneous up to 275°C , beyond which the rest of the line narrows rapidly. The T_1 of NaMgH_3 is a few seconds, remarkably short for such a ‘rigid’ spin system; presumably, a large concentration of unpaired electrons are present here as well.

LiBH_4 has much faster atomic motions. At all temperatures above -100°C , the tetrahedral BH_4 units reorient rapidly, as shown in earlier work. At a solid-solid transition at 109°C , the Li^+ motion increases dramatically. As in Figure 4, the ^7Li resonance narrows so that quadrupolar satellites at $\pm 10 \text{ kHz}$ are clearly resolved. Thus, the high-temperature (HT) phase may be superionic, though the Li^+ motion is $\approx 10^9 \text{ s}^{-1}$, far below the liquid-like rates of some superionics.

The H and ^{11}B resonances also narrow from 170 – 240°C , well into the HT phase (see Figures 5, 6, and 7). The activation energy extracted from H linewidth and $T_{1\rho}$ data is 0.72 eV , $\pm 5\%$. The narrowing of the ^{11}B resonance is crucial: if the BH_4 units were not diffusing and the H were moving by exchanging between neighboring BH_4 units, the ^{11}B linewidth could not decrease below that predicted from B-B dipolar interactions. This limiting width is calculated to be 1,600 Hz, while the narrowest line in Figure 7 is 300 Hz (all values FWHM). So, the BH_4 are diffusing as intact units.

FIGURE 4.

FIGURE 5.

FIGURE 7.

FIGURE 6.

FIGURE 8.

Measurements in molten LiBH_4 at 285°C rule out rapid H-exchange between BH_4 units. As displayed in Figure 8, the ^{11}B spectrum has 5 lines of intensity ratio 1:4:6:4:1. This is unambiguous evidence that each BH_4 has long-lived spin states of the 4 H atoms (i.e., 4 up, 3 up + 1 down, 2 up + 2 down, etc.). Rapid exchange would lead to collapse (averaging, narrowing) of the 5-line pattern. From the linewidth in Figure 8, the BH_4 lifetime against H-exchange is at least 16 ms. From spin-echo experiments, the lifetime is at least several seconds. Thus, exchange in the melt is slow; in the solid the exchange will be even slower. Thus the previously observed isotopic scrambling of BH_4 , BH_3D , BH_2D_2 , etc does not occur through rapid H-exchange.

Separate NMR isotope scrambling experiments starting with mixed LiBH_4 and LiBD_4 powders find nearly complete isotopic mixing in 30 minutes or less. Thus, in the melt, H-exchange falls in between the several second and 30 minute time scales.

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People Working on DOE Project

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- Timothy Ivancic, full support.
- David T. Shane, full support.

Undergraduate student:

Charles McIntosh, summer student, 3 months.

Collaborators at other institutions:

- Ragaiy Zidan, Ashley Stowe (now at Y12, Oak Ridge), Savannah River National Laboratory.
- Son-Jong Hwang, California Inst. Of Technology, Chemistry NMR Facility, sub-contract leader.
- Jacques Huot, U. Quebec Three Rivers.
- Martin Dornheim, Rudiger Bormann, Jose Bellosta von Colbe, GKSS in Germany.

IV.I.14 First-Principles Studies of Phase Stability and Reaction Dynamics in Complex Metal Hydrides

PI: Mei-Yin Chou

Georgia Institute of Technology

Contract Number: DE-FG02-05ER46229

Report Date: April 20, 2009

Period Covered: January 1, 2008 – December 31, 2008

Project Description

Complex metal hydrides are believed to be among the most promising materials for developing hydrogen storage systems that are suitable for transportation applications. In order to facilitate the much-needed breakthroughs in this field, we plan to perform extensive theoretical studies on various properties of hydrogen in these complex hydrides. The purposes are: (1) to understand the fundamental science associated with the intrinsic materials properties of these hydrides, the hydrogen absorption and desorption dynamics, and the mechanisms of catalytic reactions; (2) to facilitate materials design and improvement; and (3) to explore novel hydrides with various compositions.

Accomplishments in 2008

(a) Phase Stability of Mixed Alkali Alanates

We have performed first-principles calculations to study the possible alloy phases of mixed sodium and lithium alanates and their structural and energetics properties. For the tetrahydrides, the energetics of the alloy $\text{Na}_{1-x}\text{Li}_x\text{AlH}_4$ is calculated and a small, positive mixing energy less than 5 kJ/mol was found for all values of x , indicating that the alloy is not stable with respect to the end compounds. The equilibrium structure undergoes a transition from a tetragonal structure to a monoclinic structure between $x = 0.25$ and 0.5. Within each structure the cell volume decreases with increasing x , which can be explained by Li having a smaller ion size than Na. In contrast, for the hexahydrides $\text{Na}_{3(1-x)}\text{Li}_{3x}\text{AlH}_6$, one stable intermediate compound $\text{Na}_2\text{LiAlH}_6$ ($x=1/3$) is found in agreement with experiment. [J. Alloys Compd., in press]

(b) Local Order in a Mixed Lithium-Magnesium Imide

Recently it was discovered that a total of 5.6 wt% H_2 could be released from the 1:2 mixture of lithium

amide and magnesium hydride at temperature as low as 150°C. With a reaction enthalpy of 44 kJ/mol- H_2 , this system has high potential for on-board hydrogen storage applications. The fully desorbed product is believed to be a mixed lithium-magnesium imide $\text{Li}_2\text{Mg}(\text{NH})_2$. Rijssenbeek et al. reported that $\text{Li}_2\text{Mg}(\text{NH})_2$ has disordered cation and vacancy arrangements at room temperature and above. We have performed first-principles calculations to investigate a series of ordered low-energy configurations for this compound. Specific local orderings are found in the cation vacancy arrangement, shedding light on the experimental disordered structure models. A possible ordered phase at low temperature is proposed based on these local orderings. The similarity and difference of local arrangements among hydrogen, cations, and vacancies are also noted for the three amide/imide systems: LiNH_2 , $\text{Mg}(\text{NH}_2)_2$, and $\text{Li}_2\text{Mg}(\text{NH})_2$. [J. Appl. Phys. **104**, 093619 (2008)]

(c) Special Binding Features in $\gamma\text{-AlH}_3$

Aluminum hydride (alane) AlH_3 is an important material in hydrogen storage applications. It is known that AlH_3 exists in multiple forms of polymorphs, where $\alpha\text{-AlH}_3$ is found to be the most stable with a hexagonal structure. Recent experimental studies on $\gamma\text{-AlH}_3$ reported an orthorhombic structure with a unique double-bridge bond between certain Al and H atoms. This was not found in $\alpha\text{-AlH}_3$ or other polymorphs. Using density functional theory, we have investigated the energetics, and the structural, electronic, and phonon vibrational properties for the newly reported $\gamma\text{-AlH}_3$ structure. The calculation concludes that $\gamma\text{-AlH}_3$ is less stable than $\alpha\text{-AlH}_3$ by 1.2 kJ/mol, with the zero-point energy included. Interesting binding features associated with the unique geometry of $\gamma\text{-AlH}_3$ are identified from the calculated electronic properties and phonon vibrational modes. The binding of H-s with higher energy Al- p , d orbitals is enhanced within the double-bridge arrangement, giving rise to a higher electronic energy for the system. Distinguishable new features in the vibrational spectrum of $\gamma\text{-AlH}_3$ were attributed to the double-bridge and hexagonal-ring structures. [Phys. Rev. B **77**, 014101 (2008)]

(d) Catalytic Effect of Near-Surface Titanium on Hydrogen Interaction on the Al(100) Surface

The critical role played by the Ti catalyst in helping hydrogen cycling in alanates remains a challenging question for this hydrogen storage material. In this study we examine the hydrogen related reactions on an Al

surface in the presence of Ti by first-principles density-functional calculations. It is found that a stable alloy TiAl_3 is formed near the Al surface with Ti occupying subsurface sites. This subsurface Ti arrangement not only enhances H binding with the Al surface layer, but also improves H mobility on the surface. Moreover, the stability of dissociated H is improved and the dissociation energy barrier is reduced. Based on these results and existing experimental data, we propose that for the dehydrogenation process the catalyst kinetically facilitates the release and decomposition of AlH_3 from solid-state alanates, and for the hydrogenation process the catalyst helps the absorption of hydrogen and the formation of AlH_3 on Al surfaces.

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3. Zhu Ma and M.Y. Chou, "First-Principles Investigation of Sodium and Lithium Alloyed Alanates," *J. Alloys Compd.* (in press).

Personnel

Zhu Ma (Graduate student, full support)
Pei Lin (Graduate student, partial support, 50%)
Yan Wang (Research scientist, partial support, 25%)
Fen Zhang (Postdoc, full support)

IV.I.15 Influence of Pressure on Physical Property of Ammonia Borane and its Re-Hydrogenation

PI: Jiuhua Chen

Florida International University

Contract Number: DE-FG02-07ER46461

Date of the report: April 23, 2009

Period covered by the report:
May 1, 2008 – April 23, 2009

Accomplishments

Characterization of the High Pressure Phase Discovered During the First Year

The newly discovered high pressure phase (at $P > 1.3$ GPa) has been indexed with a monoclinic symmetry. Table 1 shows the result of indexing. All the diffraction data of the new phase collected at 1.3, 1.6, 2.1, 3.2, 4.3 GPa were analyzed using Le Bail fitting. An example of the Le Bail analyses is shown in Figure 1. The derived molecular volumes of the new phase (with monoclinic structure and $Z=3$) at different pressures and those of tetrahedral ammonia borane before the phase transition are plotted in Figure 2. The high pressure phase is about 7% denser and nearly twice incompressible than the low pressure phase. The bulk modulus of the new high pressure phase is $K=21\pm5$ GPa while low pressure phase has $K=9.6\pm0.9$ GPa.

TABLE 1. Indexing of the pressure phase of ammonia borane at 4.3 GPa with monoclinic unit cell: $a=6.8551$ Å, $b=4.5495$ Å, $c=5.0612$ Å, $\beta=95.516^\circ$, $V=157.13$ Å³

h	k	l	d_{cal}	d_{obs}	$d_{obs}-d_{cal}$
0	1	1	3.3766	3.3909	0.0143
2	0	0	3.4120		-0.0211
1	1	-1	3.1062	3.1147	0.0085
2	0	-1	2.9590	2.9651	0.0061
2	0	1	2.7078	2.7159	0.0081
2	1	1	2.3269	2.3210	-0.0059
3	0	-1	2.1514	2.1467	-0.0048
0	2	1	2.0732	2.0735	0.0003
1	2	-1	2.0057	2.0066	0.0009
2	1	2	1.7847	1.7847	0.0000
3	2	0	1.6085	1.6000	-0.0084

FIGURE 1. Le Bail fitting of the X-ray diffraction pattern of H_3BNH_3 at 5.3 GPa. Crosses: observed data; red line: calculated data, bars: expected diffraction lines, green line: difference between observed and calculated data

FIGURE 2. Derived molecular volume of H_3BNH_3 as a function of pressure. $Z=3$ for the high pressure monoclinic phase.

Rehydrogenation of Ammonia Borane at High Pressures

Possibility of pressure induced rehydrogenation for decomposed ammonia borane was investigated using in situ Raman spectroscopy and X-ray diffraction. Ammonia borane sample was loaded in a diamond anvil cell. The pressure was slightly raised to generate a close system (sealed system) to retain the hydrogen released during decomposition. The sample temperature was then increased to start the thermolysis of ammonia borane. The decomposed products were quenched to ambient temperature, and then subject to further pressurization.

Figure 3 shows the X-ray diffraction patterns collected during the experiment. The sample was

FIGURE 3. Raman spectra of ammonia in a close system (DAC cell) during heating and compression. Data sequence starts from the top spectrum at ambient conditions, and follow by increasing in temperature at 0.8 GPa to 300°C, and then compression after cooling. (: vibration modes from ammonia borane, H₂: vibration from molecular hydrogen)

heated at 0.3 GPa up to 150°C, at which diffraction peaks from ammonia borane phase totally vanished. The sample was then quenched and compressed up to 9 GPa. At 8.1 GPa, weak peaks appeared at the location where ammonia borane diffraction peaks are expected. Nevertheless, intensities of these peaks were very weak comparing to the diffraction from initial ammonia borane sample in the cell. Similar experiments were conducted using Raman spectroscopy. Figure 4 shows the Raman spectra of B-H and N-H vibration regions during the heating and compression. The strongest peak at about 1,350 cm⁻¹ is from diamond anvil. The sample was heated at 0.8 GPa (8 kbar), up to 300°C. B-H and N-H rocking (12), B-H stretching peaks (5 and 5') totally disappeared when temperature was increased to 300°C, companied by appearance of H₂ molecule vibration. Upon compression to about 10 GPa (~98 kbar), these peaks came back with significantly weakened intensities.

These experiments indicate that pressure might promote the reversal of the thermolysis process.

FIGURE 4. X-ray diffraction patterns of ammonia borane during heating (starts from top spectrum) and compression. Arrows represent peaks from ammonia borane. Dots indicate possible re-occurrence of the ammonia borane peaks.

Possible leak of the released hydrogen (evidenced by weakening of the H₂ molecule vibration peaks) may give rise to the extremely weak signal of the reversed process.

Study of Possible Formation of New Phase that Contains Higher Hydrogen Content than Ammonia Borane at High Pressure

To explore possible phase that may contain more hydrogen than ammonia borane, we have conducted experiments to study the reaction of ammonia borane and hydrogen at high pressures (Part of the work was led by Wendy Mao of the Stanford University team). Ammonia borane was loaded in a diamond anvil cell with high pressure hydrogen gas (~2 kbar). The sample was then compressed to high pressures. Figure 5 show comparison of the X-ray diffractions between the samples loaded with and without hydrogen gas (labeled as AB-H₂ and pure AB respectively) at about 9 GPa. A significant difference in the diffraction patterns between the two samples was observed, indicating a possible reaction between ammonia borane and H₂ at high pressure. This reaction is anticipated to produce a phase with higher hydrogen content than ammonia borane. Raman spectroscopy conducted at FIU also indicates some changes in the spectra when mixture of ammonia borane and H₂ undergoes high pressure (Figure 6). The broad peak at 2,900 cm⁻¹ is expected

FIGURE 5. Comparison of X-ray diffraction patterns from ammonia borane + hydrogen gas and from pure ammonia borane in a diamond anvil cell at high pressure.

FIGURE 6. Raman spectra of ammonia borane + hydrogen gas in a diamond anvil cell at high pressure. Sample was heated up to 89°C after initial loading. NH_4^+ indicate possible formation of NH_4^+ species in the sample.

to be caused vibrations of NH_4^+ group. If such an assignment is valid, this indicates that the reaction between ammonia borane and molecular hydrogen yields NH_4^+ containing species.

Study of Ammonia Borane at Low Temperature and High Pressure

Stability of ammonia borane at low temperature and high pressure was investigated using in situ X-ray diffraction. A diamond anvil cell loaded with ammonia borane sample was placed in a helium cryostat. The whole cell is cooled from ambient temperature down to 9.5 K. X-ray diffraction from ammonia borane sample was collected during cooling. Phase transition from the tetragonal to orthorhombic structure was observed at

FIGURE 7. X-ray diffraction patterns of ammonia borane in a diamond anvil cell during (a) cooling and (b) compression at low temperature (9.5 K). The phase transition from tetragonal to orthorhombic structure happens at 189 K.

189 K (Figure 7a). The orthorhombic phase is stable till 9.5 K. Compress of the sample at 9.5 K did not produce any other phase transformation up to 2.1 GPa (Figure 7b).

Influence of Metal Substitution in Ammonia Borane

One issue in the reversibility of the thermolysis process is polymerization of decomposed product, $-(\text{H}_2\text{BNH}_2)_n-$. Substitution of H by alkali metals might be helpful. We have tried to substitute H with Li, Na and Mg by ball milling mixture of H_3BNH_3 and LiH (1:1 mole ratio), H_3BNH_3 and NaH (1:1 mole ratio), H_3BNH_3 , NaH and LiH (2:1:1 mole ratio), H_3BNH_3 , LiH and MgH_2 (3:1:1 mole ratio). Figure 8 shows the X-ray diffraction patterns of the products. Ball milling (1-2 hr) mixture of H_3BNH_3 and LiH produces LiH_2BNH_3 . In the case of H_3BNH_3 and NaH, NaH_2BNH_3 can be produced by ball milling, but decomposition NaH_2BNH_3 may occur during over time (>1 hr) ball milling. An unreported phase was produced from the mixture of H_3BNH_3 , LiH and MgH_2 . Chemistry and structure of this new phase is under investigation.

FIGURE 8. X-ray diffraction patterns of samples after ball milling. The starting composition and ball milling time are indicated in the next to the patterns.

Thermogravimetric measurements (Figure 9) show that LiH_2BNH_3 releases hydrogen at a lower temperature with regard to H_3BNH_3 . The new phase formed from H_3BNH_3 , LiH and MgH_2 loses more than 30% weight upon heating to 170°C (Figure 10). Likely certain amount of NH_3 is released during the heating.

Other Related Studies on Boron Compounds and Metal Hydrides

We also investigated regeneration of ammonia borane through other boron compounds. Previous studies showed that the treatment of B–O species with strong reducing agents such as sodium hydride can lead to the formation of B–H bonds, as demonstrated in the well-known Schlesinger process for the synthesis of NaBH_4 from $\text{B}(\text{OH})_3$. This process is however neither

FIGURE 9. Result of thermogravimetric measurement of LiH_2BNH_3 . TG curve is plotted on the primary axis and DSC is plotted on the secondary axis.

FIGURE 10. Result of thermogravimetric measurement of ball milling product from H_3BNH_3 , LiH and MgH_2 (3:1:1 mole ratio). Axis note is the same as Figure 9.

efficient nor optimal. An effort led by Yusheng Zhao of the Los Alamos team was made to explore a new approach of ammonia borane regeneration from the $B(OH)_3$ using high H_2 pressure with the reaction shown below:

This work is currently underway, and the reaction product is to be characterized by XRD. We also plan to use catalysis such as Pt to convert the high-pressure H_2 into hydrogen atoms, a process that can conceivably optimize the regeneration reaction.

Behavior of boron, boron suboxide, $NaBH_4$, $BH_3N_2H_4$ and metal hydrides e.g. Mg_2FeH_6 and AlH_3 at high pressures were also investigated. Due to the limited space, here we describe a summary for $NaBH_4$ and AlH_3 as examples. We have studied structural stability of $NaBH_4$ under high pressures up to 14 GPa (temperatures up to 425°C) using in situ X-ray diffraction and 27 GPa (ambient temperature) using in situ Raman spectroscopy. An extended high P-T phase diagram is constructed (Figure 11). Bulk modulus, its temperature derivative and thermal expansion coefficient for the cubic phase are found to be 17.5(5) GPa, -0.0137 GPa/K and $12.06 \times 10^{-5} + 26.75 \times 10^{-8}T$, respectively. In situ X-ray diffraction of AlH_3 at high pressures revealed a new structural phase transition from γ - AlH_3 at 13.5 GPa (Figure 12). Among the three forms of AlH_3 (α , β , γ) that can be produced at ambient conditions, α - AlH_3 did not transform to this new phase upon compression. Compressibility of the three phases were also measured (Figure 13).

FIGURE 11. Derived phase diagram of $NaBH_4$ from in situ X-ray diffraction and Raman spectroscopy.

FIGURE 12. X-ray diffraction of AlH_3 during compression. Symbols "••" and "*" marks the strongest peaks of β - AlH_3 and γ - AlH_3 phases, respectively, arrows show peaks of the new high pressure phase.

FIGURE 13. Volume (V/V_0) of α -, β - and γ - AlH_3 as a function of pressure, derived from in situ X-ray diffraction.

A List of Papers in which DOE Support is Acknowledged

Journals:

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2. Jiuhua Chen, Yunpeng Yang, Tony Yu, Jianzhong Zhang, Yusheng Zhao and Liping Wang, Strength measurement of boron suboxide B_2O_3 at high pressure and temperature using in situ synchrotron X-ray diffraction, *High Pressure Research*, 28(3), 423-430 (2008).
3. Lyci George, Vadym Drozd, Andriy Durygin, Jiuhua Chen, Surendra K. Saxena, Bulk modulus and thermal expansion coefficient of mechanochemically synthesized Mg_2FeH_6 from high temperature and high pressure studies, *International Journal of Hydrogen Energy* 34 (2009) 3410 – 3416.
4. Artem R. Oganov, Jiuhua Chen, Carlo Gatti, Yanzhang Ma, Yanming Ma, Colin W. Glass, Zhenxian Liu, Tony Yu, Oleksandr O. Kurakevych, and Vladimir L. Solozhenko, Ionic high-pressure form of elemental boron, *Nature* 457, 863-867, doi:10.1038/nature07736 (2009).

Presentations:

1. Jiuhua Chen, Vadym Drozd and Luke Daemen, Pressure Induced Phase Transition in Ammonia Borane, presentation at *Advances in High-Pressure Science Using Synchrotron X-rays Workshop*, Upton, New York, October 4, 2008.
2. Yu Lin, Wendy Mao and Jiuhua Chen, Raman spectroscopic studies of ammonia borane at high pressure, presentation at *2008 COMPRES annual meeting*, Colorado Springs, Colorado, June 25–28, 2008.
3. Jiuhua Chen, Vadym Drozd and Surendra Saxena, Ammonia Borane as Hydrogen Storage Material, presentation at Hydrogen Storage Symposium of the Fifth International Meeting of the Study of Matter at Extreme Conditions, Miami - Western Caribbean. March 28 – April 2, 2009.

A List of People Working on the Project – Graduate Students, Postdocs, Visitors, Technicians

Graduate students:

Srinija Rappel (50%)
Jennifer Girard (50%)
Yu Lin (travel support)

Associate:

Jozsef Garai (50%)

Postocs:

Helene Couvy (80%)
Vadym Drozd (80%)

*The experiments were conducted at the Advanced Photon Source of Argonne National Lab, National Synchrotron Light Source of Brookhaven National Lab, Cornell High Energy Synchrotron Source (CHESS) in Cornell University, Los Alamos National Lab, Stanford University and Florida International University by the collaboration team of the project.

*References are not listed due to the space limit

IV.I.16 Atomistic Mechanisms of Metal-Assisted Hydrogen Storage in Nanostructured Carbon

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Cristian I. Contescu, James Morris,
Takeshi Egami, Steven Pennycook
Oak Ridge National Laboratory
Oak Ridge, TN 37831-6087

Contract Number: ERKCM43

Date: April 2009

Period covered: 2007 – 2009

Project Scope

The goal of this project is to establish the scientific basis for designing the building blocks of carbon-based adsorbents that enable synergistic metal-carbon interactions, leading to enhanced hydrogen uptake at near-ambient temperatures. Our preliminary results suggest that addition of transition metal catalysts to nanoporous carbons with controlled nanoscale structure and porosity results in enhanced H_2 adsorption. This appears to result from as yet poorly understood atomic-scale interactions between molecular H_2 , metal particles, and carbon with proper nanostructures. Theoretical calculations demonstrate that uptake may be significantly increased if sufficient control of the structure can be attained. To optimize the design of such nanostructure, it is essential to develop atomistic models that realistically describe isotropic nanoporous carbons and to gain fundamental understanding, at the atomic and molecular level, of hydrogen interactions within metal-doped carbons. The project is focused on three specific aims: (1) modeling and characterization of medium-range order in partially amorphous – partially graphitic structures of nanoporous carbons; (2) understanding the mechanism of molecular activation of H_2 by metal particles; and (3) elucidation of the energetics and dynamics of hydrogen species confined in the molecular space of pure- and metal-doped nanoporous carbons.

Understanding and Modeling the Local Structure of Nanoporous Carbons and their Role on Hydrogen Storage

The lack of a fundamental understanding of structure-chemistry relationships has hindered a breakthrough in hydrogen storage capability in nanoporous carbon materials. Our focus in this task is on developing realistic and comprehensive models

of the structure of nanoporous carbons that allow us to understand the role of the local atomic structure, compositional changes, and degree of order on the mechanisms of hydrogen adsorption. This is a real challenge due to the lack of a clear atomic picture of the nanopores present in these important materials, and the degree to which preparation methods and metal additions may change the structure.

As an initial effort to model adsorption, and to identify local structures that assist in adsorption, we theoretically investigated the effect of interlayer spacing between graphite layers on the hydrogen uptake [1]. The weak binding of H_2 on individual graphene sheets cannot support significant storage at ambient temperature. On the other hand, the interlayer spacing in crystalline graphite (0.335 nm) is too narrow to accommodate H_2 molecules (0.406 nm). While some absorption would be possible if the interlayer spacing were allowed to expand [2,3], the layers are not free to expand significantly, and this limits the total absorption. Our ab-initio calculations indicated that it might be possible to store H_2 molecules between graphene layers if the difficulty associated with the high energy barrier for uptake of H_2 at the initial absorption stage could be overcome. Once the “initial” H_2 molecules are absorbed, further lattice expansion is induced, which enables further H_2 absorption. An optimal expansion near 60% was found, as shown in Figure 1. Graphite structures with pre-expanded interlayer spacing could be obtained by intercalation of metal atoms or other spacer molecules, or by cross-linked hydrocarbons with the appropriate geometries. In addition, slit-

FIGURE 1. Grand Canonical Monte Carlo results (GCMC) for hydrogen uptake in expanded graphite as a function of interlayer spacing [1].

shaped pores in nanoporous carbons [4] having widths in the range of ~ 0.6 nm (i.e. about 60% expansion of graphite interlayer) would also exhibit significant uptake at equilibrium. Our calculations also show that the stacking sequence makes important changes in the binding energy: changing from the normal A-B stacking in graphite to an A-A stacking lowers the energy significantly, roughly by $\sim k_B T$ per molecule at ambient conditions, making the interaction stronger. This suggests that changes in local structure (such as stacking sequence and relative position of atoms) can have a dramatic change in adsorption.

On-going work is utilizing tight-binding molecular dynamics (TBMD) to examine possible amorphous structures, and comparing these with both high-resolution microscopy and careful diffraction studies being performed at ORNL. TBMD studies of amorphous carbon have already been demonstrated to produce results consistent with diffraction results. However, the atomic structure appears different from the partially graphitic structure observed in the high resolution microscopy obtained at ORNL. This demonstrates one of the fundamental complexities of the materials to be addressed in the current work: a simple categorization of “low density” or “three-fold” coordination fails to capture the range of experimental structures. Ultimately, the goal is to examine the adsorption of hydrogen in nanoporous carbon, using structures derived from molecular dynamics (MD) simulation (validated through diffraction experiments) in combination with Grand Canonical Monte Carlo (GCMC) simulations. We will examine not only the total adsorption capacity, but also the optimal sites for adsorption, and the structure distribution of adsorption enthalpies in the amorphous carbon. This will be done as a function of pressure and temperature, and also as a function of the structure of the amorphous carbon: different densities, graphitic order, and chemically bonded hydrogen may change the adsorption capacity significantly.

Quantitative Structural Characterization of Porous, Disordered Carbons

Nanoporous carbons are obtained through a complex sequence of elimination, cross-linking and condensation reactions during the carbonization stage, followed by selective etching and porosity development during activation. Therefore, nanoporous carbons should not be considered simply as geometrically modified graphite. Atomic level disorder that happens to be brought about by the process of making porous carbon can fundamentally change the arrangement of structural elements (graphenes, carbon bridges) and by controlling this process we can create/design new materials. Thus, very careful studies are required to

achieve meaningful characterization of such a complex structure.

The atomic pair-density function (PDF) describes the distribution of the distances between atoms in a material, and it is obtained by Fourier-transforming the structure function $S(Q)$, which is acquired from the synchrotron X-ray or neutron diffraction measurement (Q is a scattering vector). We have investigated the local atomic structure, using PDF analysis, of two carbon materials: activated carbon fibers (ACF) produced from a dense gas extracted pitch [5], and ultramicroporous carbon (UMC) obtained through chemical activation of a wood-derived precursor using KOH.

Experimental X-ray diffraction data were collected using the high energy beamline 6-ID-D, at the Advanced Photon Source, Argonne National Laboratory. The reduced PDF obtained by Fourier transformation of the structure function $S(Q)$ is shown in Figure 2. The data shows that the first few peaks are common for both samples indicating similarity in the local structure. However, significant differences are observed in the range 5-7 Å. This may be related to pores sizes or interlayer defects; both could be significant for the ability to store hydrogen. Comparison with the ideal graphite structure reveals that stacking of layers in ACF and UMC carbons resembles the rhombohedral variation of the structure (R-3m), and not the commonly observed hexagonal (P63/mmc) structure. For further structural characterization, we plan two experiments to improve the accuracy and quality of data:

- X-ray scattering using focused beam. Packing efficiency of carbons is small and significant scattering comes from air. Focused beam will improve ratio of carbon/air scattering and therefore the signal to noise ratio in diffracted intensity.
- Neutron scattering at a pulsed neutron source (Los Alamos): Neutron scattering length does not depend on the scattering vector (like X-ray scattering factor) therefore more elastic scattering is present at the high Q range. This makes normalization

FIGURE 2. Pair distribution function for activated carbon fibers (ACF) and ultramicroporous carbon (UMC).

and Fourier transformation more reliable. Also the NPDF spectrometer at Los Alamos allows for measurement at 8-10 K, thereby reducing the contribution from thermal vibrations and improving resolution of the PDF analysis.

Understanding the Role of Metals in the Storage Capacity of Nanostructured Carbons

Understanding the synergistic interaction between metals and carbon is a key factor for successful development of metal-doped carbon materials for hydrogen storage applications at near ambient temperatures. At ORNL, the effort is directed at investigation of activated carbon fibers (ACF) modified with nanoparticles of a noble metal (Pd) dispersed in its nanostructured matrix. The Pd-ACF materials are synthesized and activated in collaboration with Clemson University[6]. Characterization by aberration-corrected, high resolution STEM showed that Pd is present both as small particles (~5 nm) and as isolated atoms or atom clusters [7]. The Pd-modified activated carbon fiber (Pd-ACF) showed 25-35% higher hydrogen adsorption capacity (at 25°C and 2 MPa) than pure activated carbon fiber (ACF), even after subtracting the contribution from formation of Pd hydride.

In order to understand the origin of enhanced hydrogen capacity of Pd-ACF, we investigated, separately, the effect of carbon on the H₂-Pd interaction, and the effect of palladium on the H₂-carbon interaction. The H₂-Pd interaction was monitored using in situ high-pressure XRD and adsorption studies. The results showed that two factors contribute to destabilization of the hydrogen-rich β -PdH_{0.67} hydride: an increase in number of Pd-carbon contacts, and cleaning residual oxygen from the carbon surface. This is illustrated in Figure 3 which shows the effect of H₂ on phase equilibrium between β and α Pd hydrides [8]. On the other hand, using inelastic neutron scattering to monitor the H₂-carbon interaction showed that new C-H bonds were slowly formed at room temperature

when carbon was exposed to hydrogen in presence of Pd. This demonstrates that atomic H was formed on the surface of Pd-ACF in presence of hydrogen [9]. In combination, these two results revealed that oxygen-free nanostructured carbons have the capacity to ‘pump-out’ hydrogen from β -PdH_x, and that the ‘pumped-out’ hydrogen occupies energetically favorable sites on carbon. In other words, these studies have isolated two elementary steps in the chain of events that compose the hydrogen spillover mechanism: (1) dissociation of molecular H₂ and (2) chemisorption to chemically unsaturated positions (dangling bonds) on the carbon surface. Based on the scale of the various effects, it appears that the contribution of spillover is secondary to physisorption, at least for Pd-ACF at near-ambient temperatures.

Recently we have also evaluated the H₂ adsorption properties at room temperature of an ultramicroporous carbon (UMC) obtained by activation of a wood-derived precursor using KOH. Analysis by PDF (Figure 2) revealed that this material has a distorted stacking sequence, while chemical analysis showed presence of alkali metals (Na, K) remnant after chemical activation. Adsorption measurements at room temperature showed an outstanding H₂ capacity and unusually large adsorption energy. We are currently investigating whether the presence of alkali metals, and the carbon structure resulting from KOH activation, contribute synergistically to polarization-induced enhanced physisorption of hydrogen. At the same time, we are investigating the hypothesis that Pd could be used as a source for hydrogen spillover in order to substantially accelerate the rate of adsorption.

Both ACF and UMC are derived from natural sources, petroleum pitch and wood, respectively. All carbon materials from natural sources inherently have uncontrolled composition and structure, along with trace impurities that might influence the hydrogen uptake. In order to eliminate such possibilities, we are now using a synthetic polymer, polyfurfuryl alcohol (PFA), as the source of carbon. Initial tests have shown that

FIGURE 3. Room temperature XRD patterns of Pd-ACF (a), commercial Pd-carbon catalyst (b), and Pd-black (c) as a function of P_{H_2} . The peaks correspond to (111) diffraction of α and β -PdH_x phases. Note that, with the decrease in the degree of Pd-C contacts, the equilibrium transition pressure decreases (marked with a black line). [8]

it is possible to synthesize nanostructured carbon with reproducible properties by controlling the conditions during polymerization, carbonization, and physical activation. Room-temperature adsorption of hydrogen on activated PFA-derived carbon (PFAC) showed that the hydrogen uptake capacity nearly equals that of ACF. The next step is doping this carbon with metals in order to understand and control the mechanisms that influence the hydrogen uptake properties of metal-modified nanostructured carbon materials.

List of Publications and Extended Abstracts

Journal Publications

1. Rachel S Aga, Chong Long Fu, Maja Krcmar, James R. Morris "The effect of graphite interlayer spacing on hydrogen absorption" *Phys Rev B* **76** (2007) 165404.
2. Xianxian Wu, Nidia C. Gallego, Cristian I. Contescu, Halil Tekinalp, Vinay V. Bhat, Frederick S. Baker, Mark C. Thies "The effect of processing conditions on microstructure of Pd-containing activated carbon fibers" *Carbon* **46** (2008) 54-61.
3. Cristian I. Contescu, Craig Brown, Yun Liu, Vinay V. Bhat, Nidia C. Gallego "Detection of hydrogen spillover in palladium-modified activated carbon fibers during hydrogen adsorption" *J. Phys. Chem. C* **113** (2009) 5886-5890.
4. Klaus van Benthem, Stephen J Pennycook "Electron microscopy at very high resolution" in "*Dekker Encyclopedia of Nanoscience and Nanotechnology*", CRC Press, 2009, vol. 2, p. 1217.
5. Xianxian Wu, Nidia C. Gallego "Carbon-based nanostructures: Hydrogen storage" in "*Dekker Encyclopedia of Nanoscience and Nanotechnology*", CRC Press, 2009, vol. 1, p. 535.
6. Vinay V. Bhat, Cristian I. Contescu, Nidia C. Gallego "The role of destabilization of palladium hydride on the hydrogen uptake of Pd-containing activated carbons" *Nanotechnology* **20** (2009) 204011 (Special Issue on Nanoscale Phenomena in Hydrogen Storage).
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11. Cristian I. Contescu, Vinay V. Bhat, Nidia C. Gallego: "Hydrogen spillover: Its 'diffusion' from catalysis to hydrogen storage community", in *Prepr. Pap. -Am. Chem. Soc., Div. Fuel Chem.* **2009**, 54 (1), 382-383.

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Extended Abstracts

1. H.L. Tekinalp, E. Cervo, M.C. Thies, C.I. Contescu, N.C. Gallego, D.D. Edie; "The effect of pitch composition on the adsorption behavior of Pd-doped ACF", *Proc. CARBON 2007 International Conference*, July 15-20, 2007, Seattle, WA.
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- Rachel Aga, Alloying Behavior and Design Group, ORNL (2005-2008), Partial support.

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IV.I.17 Application of Neutron Scattering on Hydrogen Storage

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Oak Ridge National Laboratory

Contract Number: ERKCC01- Oak Ridge
National Laboratory

Reporting period: 2007-2009 April 24, 2009

Recent Progress

The hydrogen activities described below represent a subset of a larger FWP (ERKCC01) identified above. That effort couples synthesis, advanced characterization (including neutron scattering) and computational and theoretical modeling. The primary objective is to discover and exploit controlled synthetic methods to produce, characterize and ultimately control novel inorganic nanometer-scale materials and to gain a fundamental understanding of how the spatial or temporal confinement of atomic or molecular species onto or within materials impact the physicochemical properties. These objectives are achieved using advanced characterization methods unique to the ORNL environment, including the world's brightest spallation neutron source (SNS), state-of-the-art, aberration-corrected, Z-contrast, scanning transmission electron microscopes with 1 Å or finer resolution, leadership-class computing capabilities as represented by petascale computers like Kraken and Jaguar, and the Center for Nanophase Materials Sciences (CNMS), combined with a team of expert personnel uniquely qualified to exploit these resources.

Hydrogen Interactions with Metal Oxide (MO) and Carbonaceous Material

We used inelastic neutron scattering (INS) spectroscopy techniques to obtain detailed information about H₂ interactions with a prototypical MO surface, i.e. MgO (100). INS techniques are *unrivalled* in sensitivity and precision for probing the rovibrational dynamics of condensed phase H₂ molecules [Mitchell, 2005]. They present several advantages over infrared spectroscopic and helium atom scattering methods for interrogating the dynamics of H₂ adsorbates: neutron scattering does not depend on the weak transition dipole moment induced in H₂ adsorbates by the underlying surface (i.e., no optical selection rules), neutrons can penetrate deeply through bulk matter to provide information about adsorbate dynamics in the multilayer adsorption regime, and, unlike infrared or helium atom scattering techniques, INS spectroscopy

can directly probe the para→ortho ($J=0 \rightarrow 1$) transition of H₂ adsorbates. INS studies of monolayer and multilayer H₂ films adsorbed on nearly defect-free MgO (100) surfaces were performed and interpreted with the aid of a reduced dimensionality quantum dynamical model for the H₂ adsorbates. Our studies show that, for this system, the $J=0 \rightarrow 1$ rotational transition previously observed in INS studies of both bulk H₂ and H₂ adsorbed on carbon-based materials is shifted to substantially lower energy due to interactions between the H₂ films and the MgO (100) surface. Our findings suggest that these interactions substantially hinder the adsorbates' end-over-end rotational motion enough that the first-layer H₂ molecules acquire partial two-dimensional (2D) character. These studies are made possible by the size-selectable, chemically pure, MgO nanocubes produced by our patented process (Kunmann-Larese U.S. Patent #6.179.897, 2001) that involves decomposition of an intermediate Mg carbide phase. Detailed high-resolution thermodynamic studies (Frazier, PhD thesis UTK 2008) have provided a roadmap for exploring the phase diagram. At submonolayer coverage H₂ forms a commensurate c(2x2) phase. An increase in the monolayer surface density results in a devil's staircase set of transitions involving uniaxially compressed p(2x4) and p(2x6) solids. At monolayer completion, a hexagonal solid form that is 25% more dense than the closed-packed phase of bulk H₂ at the same temperatures (see Figure 1). Our INS results indicate, and our computational studies substantiate, that the INS feature observed at 11.3 meV using H₂ and 8.0 meV using HD, is associated with hindered, quasipolar rotational motion of molecular hydrogen adsorbed atop Mg²⁺ cations on the MgO (100) surface (see Figure 2). For reference, we include in Figure 2 the INS response of a commensurate ($\sqrt{3} \times \sqrt{3}$ R 30°) monolayer of H₂ on the basal plane of graphite, which exhibits the same unhindered rotational motion as the H₂ bulk solid or gas phase (i.e. the para→ortho transition at 14.7 meV). The melting temperature of the compressed monolayer solid appears to be about 25-30K. The combination of INS, thermodynamics, diffraction and theory has played a valuable role in understanding this fascinating system. These efforts are aimed at obtaining a quantitative model for the H₂-MgO interaction that can be used to understand H₂ adsorbate dynamics in both monolayer and multilayer films.

In addition to the interaction of hydrogen with pure MOs we have expanded our investigation to include the interaction of molecular hydrogen with nm-sized metal clusters decorating the MOs. These studies are aimed at developing a better understanding of H₂ interactions with these dispersed metal clusters and how the interaction of H₂ with the metal cluster is modified

FIGURE 1. Neutron diffraction profiles (a) and (b) and schematics of solid structures (c) and (d) for c(2x2) submonolayer (c) and complete monolayer (d).

FIGURE 2. INS spectra collected using TOSCA spectrometer at ISIS spallation source. The individual spectra are the INS response from monolayer films.

FIGURE 3. STEM micrographs of Pd decorated (left) MgO nanocubes and (center) ZnO tetrapod and (right) ZnO/Pd interface. The Pd nm particle is at the right of the figure.

by the MO support. We want to determine what role the MO plays in stabilizing the nm scale metal cluster and how the physicochemical properties of the metal (and/or the support) are changed. MOs are routinely used for supports for catalysts and we are interested to see how the crystal and electronic structure of the metal cluster is affected by the adjacent MO interface. Our latest investigations focused on synthesis and characterization of Pd decorated ZnO and MgO nanoparticles. Figure 3 shows representative electron micrographs of the Pd decorated nanomaterials. It is especially interesting to note the high-resolution image of the Pd-ZnO interface where the interface is easily resolved. Preliminary analysis of photoemission measurements for the nm Pd clusters on the ZnO indicate that the Pd3d core level spectrum appear to be unshifted from bulk Pd metal, however, a more careful examination of the results are underway. Furthermore, preliminary INS measurements of H₂ adsorption on the Pd decorated ZnO suggest that all of the H₂ molecules adsorb *molecularly* (i.e. below saturation) at the Pd sites and that the bound length increases by ~6% based on the shift of the para→ortho transition energy to lower values.

Modeling of H₂ with nm-Scale Metal Decorated Metal Oxide Particles

The adsorption properties of molecular H₂ with Pd and ZnO and Pd decorated ZnO are currently being investigated using *ab initio* calculations with the Siesta implementation of density functional theory (DFT) within the local spin density approximation (LSDA) for the exchange and correlation functional.

Modeling of pristine ZnO and Pd surfaces confirms that upon exposure to gaseous H₂, the molecule dissociates and a hydride layer is formed. For the Pd nanoparticle(cluster), the preferred absorption site is in the center of the triangles formed by the close-packed Pd atoms, which are in the face centered cubic (FCC) configuration. For the ZnO, each of the hydrogen atoms is attached to either a Zn or an O atom (see Figure 4).

The DFT modeling of the adsorption of H₂ in Pd decorated ZnO structures is under development. Currently, our studies focus on understanding the

FIGURE 4. Evolution of the absorption of hydrogen in a palladium nanoparticle (a,b) and a zinc oxide surface (c,d). (a,c) are the initial states, and (b,d) final states.

interaction of the Pd nanoparticle with the ZnO host before we address the H_2 adsorption modeling thus mimicking the experimental procedure. Hence, the interactions of two different surfaces of the Pd cluster with three surfaces of the ZnO were investigated, produces six different configurations to be studied.

Consideration of these six configurations, coupled with an ~ 1 nm Pd cluster size and the minimum thickness of the ZnO slab to reproduce surface effects, have resulted in a highly demanding computational effort, where each system is formed by about 650 atoms.

To address this computational limitation, we have also modeled a Pd cluster deposited on of a ZnO nanorod to explore the interaction of these systems in a smaller system. In this case, the computational speed has improved; we observe that the first four layers of atoms rearrange, some atoms that comprise the first ZnO layer “attach” to the side of the Pd nanoparticle (i.e. the particle is ‘wet’ by the host), indicating a high affinity for the absorption of the Pd nanoparticle (see Figure 5). We note the general similarity to high-resolution micrograph in Figure 3.

Currently our modeling is still incomplete, computationally the system is not yet fully relaxed. The H_2 adsorption studies will be performed when the Pd/ZnO system is relaxed. However, semi empirical calculations of the combined system show that charge transfer effects cause hydrogen to stretch by about 15% and adsorb in the surface of the Pd cluster, in general accord with the experimental results.

FIGURE 5. Nanoparticle deposited upon a ZnO nanorod. The wetting of the Pd particle is observed in the displacement of the Zn and O atoms in the vicinity.

Published Papers/Thesis citing BES support

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IV.I.18 A Synergistic Approach to the Development of New Hydrogen Storage Materials, Part II: Nanostructured Materials

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The Berkeley Hydrogen Storage project consists of a broad-based, multi-investigator effort for developing new types of hydrogen storage materials. In particular, materials with the potential for meeting the 2010 DOE target of a reversible uptake of 6% H₂ by mass are sought. Our approach is to explore numerous possibilities for new materials, and narrow our focus as the research progresses. The synergy of many scientists in one location working toward a common goal is expected to accelerate our progress and lead to new ideas via cross-fertilization. One half of the project (Part I, currently funded through EERE) involves development of microporous metal-organic frameworks and polymers, as well as destabilized metal hydrides. The other half of the project (Part II, detailed here) focuses on the development of new nanostructured materials of potential utility in hydrogen storage applications. Specific areas under investigation include: the synthesis of new nanostructured boron nitride materials, computational work leading to the prediction of carbon boron nitride-containing structures with a high affinity for H₂, synthesis and evaluation of hydrogen uptake in magnesium-intermetallic nanocrystalline networks, and the development and characterization of nanocrystal/metal-organic framework hybrid materials exhibiting room-temperature hydrogen uptake via a spillover mechanism. A hydrogen storage characterization facility containing one gravimetric and two volumetric high-pressure adsorption analyzers has been created in order to provide accurate and immediate feedback on the properties of the many new materials generated.

Nanostructured Boron Nitride

Experimental efforts to explore the use of nanostructured boron nitride are being undertaken

to complement the extensive work underway on nanostructured carbon. Both chemical vapor deposition and induction furnace methods have been refined for the large-scale synthesis of pure boron nitride nanotubes. Conditions for varying the morphology of nanostructured boron nitride have been identified. Testing of hydrogen storage properties is in progress to compare the effects of different morphologies, as well as with carbon-based analogues. Chemical vapor deposition methods have also been developed for the generation of composites of boron nitride nanostructured materials and metal or metal oxide nanoparticles. These studies include the synthesis of both boron nitride nanotubes (BNNTs) and activated boron nitride nanostructured material, and also boron carbon nitride (BCN) nanotubes and related nanostructured BCN material. Computational efforts have demonstrated a higher hydrogen binding affinity for boron nitride nanotubes compared to carbon nanotubes. In addition, the role of defect structures in enhancing hydrogen binding has been explored. The results have led to an experimental effort in which carbon atoms are implanted within high-defect boron nitride nanotubes using a hydrocarbon plasma.

Methods have also been developed recently to extensively functionalize the surface of both carbon and boron nitride nanostructured materials allowing tunable interaction with a diverse range of materials for the preparation of hybrid and composite nanostructured materials. Specifically, the surfaces of boron nitride nanotubes have been functionalized with amine groups via ammonia plasma irradiation. The functionalized tubes were characterized by Fourier transform infrared spectroscopy and electron energy loss spectroscopy. The resulting amine-functionalized BNNTs were found to be highly dispersible in chloroform, and are predicted to form the basis of a new class of chemically reactive nanostructures.

Building on these capabilities, solution chemical routes to depositing a diverse range of metal and semiconductor nanocrystals, nanorods and quantum dots on the carbon and boron nitride nanotubes have been developed. The principle example of this strategy is the decoration of BNNTs with 4-nm gold nanocrystals (see Figure 1). Gold nanoparticles were self-assembled at the surface of both amine- and thiol-functionalized boron nitride nanotubes (BNNTs) in solution. The chemical functionalization of the surface of the BNNTs was achieved following ammonia plasma irradiation in order to generate amine functional groups at the surface of the BNNTs. The amine-functionalized BNNTs were then covalently modified by the coupling of short-

FIGURE 1. Typical low-resolution TEM images of DMAP-stabilized gold nanoparticles self-assembled at the surface of different amine-functionalized BNNTs, where the lengths of the BNNTs shown are approximately 750 nm (a), 1 μm (b), 600 nm (c), and 100 nm (d).

chain thiol-terminated organic molecules to result in thiol-functionalized BNNTs. The functionalization of the BNNTs was characterized using XPS, FT-IR spectroscopy, and EDS, whereas the nanoparticle-nanotube assemblies were characterized using HR-TEM and EELS. This approach constitutes a basis for the preparation of highly functionalized BNNTs and their utilization as nanoscale templates for assembly and integration with other nanoscale materials. It is expected that analogous materials in which nickel or palladium nanocrystals are covalently attached to BNNTs will be of interest for the study of hydrogen storage via a spillover mechanism.

Computational Work on Nanostructured Carbon and Boron Nitride

Using first-principles calculations, we performed a search for high-capacity hydrogen storage media based on individually dispersed calcium atoms on doped or

FIGURE 2. (a) Two Ca atoms individually attached on a (7,7) pristine CNT. (b) Two Ca atoms aggregated on a pristine (7,7) CNT. (c) Initial geometry of seven H_2 molecules on the two aggregated Ca atoms. (d) Geometry of the seven H_2 molecules on the two aggregated Ca obtained from energy minimization calculation. (e) Two Ca atoms individually attached on a B-doped (7,7) CNT. (f) Two Ca atoms aggregated on a B-doped (7,7) CNT. (g) Two Ti atoms individually attached on a B-doped (7,7) CNT. Black dots indicate the Ti atoms. (h) Two Ti atoms aggregated on a B-doped (7,7) CNT. The total energy of the lower energy structure between aggregated and unaggregated structure is set to zero.

defective carbon nanotubes. We found that up to six H_2 molecules can bind to a Ca atom each with a desirable binding energy of ca. 0.2 eV/ H_2 . The hybridization of the empty Ca 3d orbitals with the H_2 σ orbitals contributes to the H_2 binding, and clustering of Ca atoms (a major problem in previous studies of using metal atoms for H_2 adsorption) is suppressed by preferential binding of Ca atoms to doped boron and defect sites dispersed on carbon nanotubes. We also found that individual Ca-decorated B-doped carbon nanotubes with a concentration of ~ 6 at% B doping can reach the gravimetric capacity of ca. 5 wt% hydrogen.

Figure 2 illustrates that, unlike transition metal atoms, Ca atom clustering is suppressed on B-doped carbon nanotubes by preferential binding of Ca atoms to B sites. Figure 3 shows the fully optimized

FIGURE 3. Side (a) and cross-sectional (b) views for the optimized atomic structure of maximal number of adsorbed H_2 molecules for a B-doped (5,5) CNT (6.25 at% of B), respectively.

structure for a maximum hydrogen-storage capacity in (5,5) carbon nanotubes with a concentration of 6.25 at% B, corresponding to 4.94 wt% uptake of H_2 , where the molecular formula may be expressed as $(C_{75}B_5 \cdot 5Ca \cdot 30H_2)_n$ with n as an integer. Up to six H_2 molecules are adsorbed on a Ca atom with the binding energy of 0.20, 0.21, 0.20, 0.19, 0.18, and 0.17 eV/ H_2 for 1, 2, 3, 4, 5, and 6 H_2 molecules, respectively, which corresponds to the desirable binding energy of H_2 molecules for room temperature hydrogen storage.

Magnesium-Based Nanocrystals

Our objectives in this portion of the project are to: (i) develop novel composite materials with high storage density and improved cycling kinetics by using a platform of nanoscale inorganic earth metals with lowered enthalpic barriers and small gas diffusion lengths relative to bulk crystals and ball-milled powders, and (ii) develop gas-selective support matrices to improve retention of sorption properties over large numbers of cycling events.

We have discovered a chemical route for generating size-controlled MgO nanocrystals. These magnesium oxide crystals are pure, single-phase crystals for which the size (2-5 nm) and surface chemistry have been carefully elucidated (see Figure 4). Detailed spectroscopic and vibrational studies have shown that we can chemically functionalize the surface with desired molecular species by solution-phase chemical exchange. We envision using these nanocrystals as precursors to size-controlled nanoscale Mg crystals for detailed H_2 sorption studies. This proposed reduction of MgO to Mg is appealing as no size-controlled route to pure Mg nanoscale crystals exists at present.

We have also worked toward development of direct chemical routes to single-phase Mg nanocrystals. Recently, our lab has successfully prepared nanocrystals of Mg nanocrystals based upon a naphthalide reduction of $MgCl_2$. Excitingly, the resultant Mg-metal product

FIGURE 4. Low (panel) and high (inset) resolution transmission electron micrograph images of MgO nanocrystals 2 nm in diameter.

FIGURE 5. X-ray powder diffraction patterns of as-prepared metallic Mg products measured as exposure time increased.

was unexpectedly stable in atmosphere and resistant to oxidation or other chemical degradation (see Figure 5).

In addition, we are working toward the preparation of Mg-nanocrystal/polymer composites with gas-selective properties. We have recently initiated studies into incorporating our Mg nanocrystals into

polymer supports to both enhance stability and provide preferential diffusion of H_2 over O_2 and H_2O , a strategy to enhance material performance over many cycles of gas uptake and release.

Nanocrystal/Metal-Organic Framework Hybrid Materials

Metal-organic frameworks (MOFs) show great potential for hydrogen storage. For example, MOF-177 stores up to 7.0 wt% H_2 at 77 K and 70 bar. While this is attributed to the microporous structure of MOFs and their associated large surface area, room temperature hydrogen storage with pristine MOFs that meets DoE requirements has not been realized. However, mixtures of MOFs with commercially available platinum on activated carbon have shown up to 4 wt% storage of H_2 at 298 K and 100 bar. The goal of this work is to investigate this phenomenon of spillover by combining MOFs and Pt nanocrystals in a controlled manner.

Firstly, we have mixed colloidally-synthesized, faceted, 10-nm Pt nanocrystals with MOF-5, MOF-177 and HKUST-1. Since these Pt nanocrystals have a polyvinyl pyrrolidone (PVP) coating, they are soluble in common organic solvents. Composites consisting of 3 wt% PVP/Pt- MOF mixtures were formed by stirring the nanocrystals with MOFs in dry dichloromethane. These composites were then degassed according to literature procedures and the surface area and hydrogen uptake were measured at 77 K. The materials exhibited a surface area slightly lower than that reported, but comparable or slightly higher hydrogen uptake at 77 K. The PVP/Pt-MOF-5 composite, however, showed hydrogen adsorption of just 0.3 wt% at 30 bar at 298 K. We plan to investigate the dependence of hydrogen storage on nanocrystal size, shape and loading.

Secondly, we have reduced Pt within a variety of metal-organic frameworks. By heating a mixture of $H_2PtCl_6 \cdot 6H_2O$ and the solid MOF in dry methanol, small Pt nanocrystals (<1 nm in diameter) can be inserted into the pores. While MOFs such as MOF-5 decompose under these conditions, HKUST-1 showed an uncompromised surface area and a slight increase in hydrogen adsorption at 77 and 87 K. We now plan to try different loadings of Pt and also use MIL-101 for this, since MIL-101 is stable in boiling water.

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4. "Size-Controlled Synthesis and Optical Properties of Monodisperse Colloidal Magnesium Oxide Nanocrystals" Moon, H.R.; Urban, J.J.; Milliron, D.J. *Angew. Chem., Int. Ed.*, submitted.

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IV.I.19 Complex Hydride Systems – a New Frontier for Future Energy Applications

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Program Scope

Hydrogen storage is one of the enabling materials technologies required to assure a successful future transition from fossil to hydrogen-based fuel. The scope of the multidisciplinary effort, which draws on considerable experimental and modeling experience and expertise at the Ames Laboratory and Virginia Commonwealth University, is to achieve a fundamental understanding of the relationships between the chemical composition, bonding, structure, microstructure, properties and performance of hydrogen-rich solids. The specific objectives of this project are to address relevant issues, which have the potential to advance basic materials science of novel hydrides and open up possibilities for their future practical use.

- Synthesize an array of novel non-transition metal-based complex hydrides where the metal, metalloid or nonmetal atom is coordinated by two to six hydrogen atoms by means of solvent-free, mechanochemical technique starting from several parent light-element hydrides.
- Fully characterize the products using state-of-the-art experimental techniques.
- Create a knowledge base relating composition, structure and properties of various classes of complex hydrides by investigating the effects of varying stoichiometry and processing history on their crystal and microscopic structure, chemical, thermodynamic and physical properties.
- Extend and refine the current understanding of the mechanisms of the solid-state transformations occurring in a few model hydrides, which is in a rudimentary state, by examining the effects of various chemical and structural modifications and processing strategies on the structure-property relationships, and dehydrogenation and hydrogenation behavior of novel non-transition metal-based complex hydrides. Special emphasis is placed on bridging lengths scales ranging from a few tenths of a nanometer (a single interatomic

distance) to microns (a single grain) and centimeters (assemblies of multiple particles varying in size, shape and structure) in order to fully explore the potential of novel solids.

- Integrate experiment with modeling and first principles theory to provide a fundamental understanding of the nature of hydrogen bonding, the structure and stability of the complex hydride phases, the effect of dopants and catalysts, temperature, and pressure in altering the nature of hydrogen-metal bond, and the role of nanostructuring on the absorption and desorption properties of hydrogen. In addition to explaining the experimental data, the theory will be used to guide experiments in search of desirable chemical composition, preparation and processing strategy, atomic scale structure and microstructure, and the nature of the substituting element(s) – all related to resultant cyclic hydrogenation and dehydrogenation properties of complex hydrides.

Recent Progress

Mechanochemically and thermochemically-induced transformations have been studied in various systems containing complex metal hydrides such as NaAlH_4 (total hydrogen content 7.4 wt%) and LiAlH_4 (10.5%), amides NaNH_2 (5.1%) and LiNH_2 (8.7%), binary metal hydrides CaH_2 (4.8%), MgH_2 (7.7%), and LiH (12.5%). Several previously unknown mechanochemical and thermochemical reactions have been discovered.

Transformations in MAlH_4 - MNH_2 systems (where $\text{M} = \text{Li}$ or Na) have been characterized using the X-ray powder diffraction, ^{27}Al , ^7Li and ^{23}Na solid state nuclear magnetic resonance (NMR) spectroscopy, transmission electron microscopy (TEM), pressure-composition-temperature (PCT) measurements and residual gas analysis (RGA). The overall mechanochemical transformations in these systems proceed as follows:

yielding from 4.3 to 6.6 wt% of hydrogen. The actual transformation mechanisms include multiple stages and intermediaries, such as Li_3AlH_6 , $\text{Na}_2\text{LiAlH}_6$, $\text{Na}_{3-x}\text{Li}_x\text{AlH}_6$ and Na_3AlH_6 . The solid state NMR analysis and TEM were used to establish the nature of the final reaction products present as a few micron size conglomerates of much smaller, 20-50 nm particles.

Unlike mechanochemical reactions, thermochemical transformations in the same systems proceed differently,

FIGURE 1. Hydrogen release during the thermal decomposition of the LiAlH_4 - LiNH_2 mixture taken in a 1:1 molar ratio.

as illustrated in Figure 1. When both M and M' are Li, the overall transformation is:

yielding a total of 9 wt% of hydrogen by weight.

The products (Equation 2) can be rehydrogenated at $P_{\text{H}_2} = 180$ bar and 275°C , and the rehydrogenation reaction is shown in Equation 3.

Mechanochemical reactions between alkali metal amides and magnesium hydride taken in 2:3 molar ratios have been investigated. Magnesium nitride, alkali metal hydrides and pure hydrogen form as end products after the high energy ball milling of the mixtures:

The amount of released hydrogen is 6.5 wt% for 2LiNH_2 - 3MgH_2 system and 5.1 wt% for 2NaNH_2 - 3MgH_2 system. Intermediate phases are MgNH and Mg_2NH with cubic structures analogous to CaNH and Ca_2NH . Mixed hydride NaMgH_3 was observed in a sodium system as one of the intermediates. The mechanism of the mechanochemical transformation in 2MNH_2 - 3MgH_2 systems can be described as follows:

Fast:

The final products of thermal decomposition of 2MNH_2 - 3MgH_3 mixtures are similar to the products

obtained via the mechanochemical route (Equation 4). The difference is only in the mechanism of the solid state transformation:

Competing reactions (Equation 8 and 12) were observed in this reaction.

Mechanochemical transformations of lithium and sodium amides with calcium hydride taken in 1:1, 1:2, 2:1 and 2:3 molar ratios, have been also investigated. Formation of calcium imide, alkali metal hydrides and gaseous hydrogen was observed for all investigated stoichiometries. In all cases, the overall mechanochemical transformations are equimolar and proceed as the following solid state reaction:

If the molar concentrations of starting materials are different from 1:1, then one of the reactants remains in excess.

Total energies and enthalpies of formation for different reaction products during the dehydrogenation of CaH_2 - MNH_2 mixtures were calculated (Table 1). It appears that mechanochemical processing (ball milling) can drive a system towards nonequilibrium configurations, resulting in different final products, and therefore, different mechanisms when compared to equilibrium dehydrogenation reactions induced by heating. Reduction of grain size, formation of structural defects, and ballistic diffusion are all believed to play a role in these nonequilibrium transformations.

TABLE 1. Enthalpies of formation for different reaction products during the dehydrogenation of CaH_2 and LiNH_2 (or NaNH_2) mixture.

Reactants	Path	Reaction Products	ΔE (eV)	ΔH (KJ/mol/ H_2)
$\text{CaH}_2 + \text{LiNH}_2$	1	$\text{CaH}_2 + \text{LiNH}_2 = \text{CaNH} + \text{LiH} + \text{H}_2$	0.560	54.032
	2	$\text{CaH}_2 + 2\text{LiNH}_2 = \text{Li}_2\text{Ca}(\text{NH})_2 + 2\text{H}_2$	1.615	77.912
	3	$\text{CaH}_2 + 2\text{LiNH}_2 = \text{CaNH} + \text{Li}_2\text{NH} + 2\text{H}_2$	1.445	69.711
	4	Step. 1: $\text{CaH}_2 + 2\text{LiNH}_2 = \text{Ca}(\text{NH}_2)_2 + 2\text{LiH}$	-0.155	
		Step. 2A: $\text{Ca}(\text{NH}_2)_2 + 2\text{LiH} = \text{CaNH} + \text{Li}_2\text{NH} + 2\text{H}_2$	1.600	77.188
		Step. 2B: $\text{Ca}(\text{NH}_2)_2 + 2\text{LiH} = \text{Li}_2\text{Ca}(\text{NH})_2 + 2\text{H}_2$	1.770	85.390
$\text{CaH}_2 + \text{NaNH}_2$	1	$\text{CaH}_2 + \text{NaNH}_2 = \text{CaNH} + \text{NaH} + \text{H}_2$	0.409	39.463
	2	$\text{CaH}_2 + 2\text{NaNH}_2 = \text{Na}_2\text{Ca}(\text{NH})_2 + 2\text{H}_2$	2.056	99.187
	3	$\text{CaH}_2 + 2\text{NaNH}_2 = \text{CaNH} + \text{Na}_2\text{NH} + 2\text{H}_2$	1.796	86.644
	4	Step. 1: $\text{CaH}_2 + 2\text{NaNH}_2 = \text{Ca}(\text{NH}_2)_2 + 2\text{NaH}$	-0.458	
		Step. 2A: $\text{Ca}(\text{NH}_2)_2 + 2\text{NaH} = \text{CaNH} + \text{Na}_2\text{NH} + 2\text{H}_2$	2.254	108.739
		Step. 2B: $\text{Ca}(\text{NH}_2)_2 + 2\text{NaH} = \text{Na}_2\text{Ca}(\text{NH})_2 + 2\text{H}_2$	2.514	121.282

Future Work

Systematic work to integrate innovative synthetic approaches with state of the art characterization and theoretical modeling will continue. Our main objectives can be summarized as follows.

- The studies of temperature induced transformations of mixed systems containing sodium alanate and sodium amide will be carried out in order to establish details of their mechanisms.
- Mechano- and thermo-chemical studies will be extended to include several new systems such as lithium and sodium borohydrides.
- The applicability and effectiveness of the mechanochemical approach as a nonequilibrium processing tool for rehydrogenation of complex hydrides under low and high hydrogen pressures and different temperatures will be thoroughly studied.
- New hybrid materials consisting of complex hydrides and intermetallic hydrogen absorbers, as well as complex hydrides supported on mesoporous carbon nanoparticles, nanotubes and fullerenes will be developed and examined.
- We will continue to employ and improve characterization methods, such as gas-volumetric analyses, PCT measurements, solid-state NMR spectroscopy, X-ray diffraction, residual gas analysis, and electron microscopy to determine to the best extent possible the structure and properties of all materials developed in this project.
- The theoretical modeling will emphasize multi-scale techniques based on density functional theory.
- As our knowledge advances, there will be an increased emphasis on integrating experiment with theory. We expect that these efforts will guide us

toward the discovery of hydrogen-containing solids that would be unattainable using conventional synthetic methods. They will also lead to a more complete understanding of both thermodynamics and kinetics of dehydrogenation and hydrogenation transformations in these materials.

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IV.I.20 Molecular Hydrogen Storage in Novel Binary Clathrate Hydrates at Near-Ambient Temperatures and Pressures

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FIGURE 1. A Conceptual Picture of Chemical-Clathrate Hybrid Storage of Hydrogen [6]

Description of Accomplishments:

1. Proof-of-Concept for Novel Chemical-Clathrate Hybrid Storage of Hydrogen

In our previous reports, we showed from X-ray and neutron diffraction, Raman and NMR spectroscopy, and gas analysis that hydrogen can stabilize several clathrate hydrate structures in the presence of different large guests. The structures include sII (tetrahydrofuran + H₂, cyclohexanone + H₂), sH (H₂ with methyl-tert-butyl ether, methylcyclohexane, 2,2,3-trimethylbutane, 1,1-dimethylcyclohexane, or isoamyl alcohol), and a semi-clathrate phase (tetra-*n*-butylammonium bromide + H₂) [1-5]. However, these double hydrogen hydrates fell short in reaching the storage capacity goal, therefore requiring that we devise a new approach to increasing the amount of hydrogen stored in the material.

We have demonstrated for the first time the proof-of-concept of chemical-clathrate hybrid storage of hydrogen using an organic compound hydroquinone [6]. This is the first storage scheme in which both molecular storage of hydrogen within hydrate cavities and chemical storage in the host molecule are utilized. Using Raman spectroscopy, we have confirmed that hydrogen molecules can be enclathrated into hydroquinone. X-ray diffraction analysis shows that in order to provide vacant cavities for the hydrogen molecules, hydroquinone undergoes a structural change from an α -phase to a β -phase under sufficient hydrogen pressure. The host molecule of this clathrate-chemical hybrid system, hydroquinone, has been also used to directly power a fuel cell [5]. At the anode side of the fuel cell, hydroquinone loses its chemically bound hydrogen in the hydroxyl group while producing electricity. This approach in taking advantage of additional chemically stored hydrogen in the host molecule promises an improvement in weight storage capacity of clathrate materials and is the first time that these two systems have been combined in a hybrid technology for hydrogen storage [6].

2. Extending the Chemical-Clathrate Hybrid Concept to a Clathrate Hydrate Hybrid System of Hydrogen

While the presence of large guests such as tetrahydrofuran (THF) and tetra-*n*-butylammonium bromide (TBAB) drastically reduces the formation pressure of hydrogen hydrate at a given temperature, weight storage capacity of hydrogen in the material also decreases because the large guests occupy the large cavities of the hydrate structure. To help overcome this trade-off between stability and weight storage capacity, the chemical-clathrate hybrid concept was applied to clathrate hydrates of hydrogen.

We have recently shown for the first time that tetra-*n*-butylammonium borohydride (TBABh) can store hydrogen both in molecular form in the hydrate cavities and chemically bound to the borohydride anion [7]. Raman spectroscopy was used to confirm the presence of encaged hydrogen in the small cages of the hydrate. X-ray diffraction revealed that the structure of TBABh + H₂ hydrate is analogous to the previously reported structure of TBAB + H₂ hydrate. An acid catalyzed hydrolysis reaction was used to produce additional hydrogen from the borohydride anion, and the reaction showed nearly 100% conversion. Using gas evolution and differential scanning calorimetry measurements, we showed that TBABh + H₂ hydrate is more stable and stores more hydrogen (27%) than the THF + H₂ hydrate system [7].

3. Raman Spectroscopic Study of Hydrogen Hydrates

Detailed Raman spectroscopic studies have been performed in order to better understand the quantum behavior of hydrogen molecules stored within the

FIGURE 2. (a) Water cavities with enclathrated TBABh and H₂ molecules. TBA⁺ is situated within the large cavities, and BH₄⁻ replaces a water molecule. H₂ is located in the small cavities. (b) Raman spectra of the H₂ vibron region in TBABh + H₂ hydrate at 76 K (top), THF + H₂ hydrate at 76 K (bottom). The similar vibrational modes of H₂ in TBABh hydrate and THF hydrate indicates H₂ is encaged in the small cavities [7].

hydrate cavities. Vibrational bands show that the molecules vibrate at lower frequencies than in the gas phase and a pair of peaks (ortho- and para-H₂) is present for each environment in the hydrogen hydrate. For a simple hydrate of hydrogen, four pairs of peaks are present for single occupancy in the small cavities and double, triple, and quadruple occupancies in the large cavities. Integrating these peaks results in an underestimation of the large cavity H₂ content, implying that a H₂ molecule in a small cavity is more polarizable than H₂ molecules in a large cavity [8].

Rotational bands show that enclathrated hydrogen molecules have orientationally dependent rotation, suggesting that the small and large cavities are orientationally anisotropic. The Raman spectrum of D₂ hydrate was also analyzed, and this indicated that D₂ was a suitable substitute for H₂ in hydrate formation. From these detailed Raman studies and complementary diffraction and gas evolution analyses, we have

FIGURE 3. The vibron region in the Raman spectrum of simple H₂ hydrate formed at 200 MPa and 250 K measured at atmospheric pressure and 76 K. 1s = 1 H₂ in a small cavity, 2L = 2 H₂ in a large cavity, 3L = 3 H₂ in a large cavity, and 4L = 4 H₂ in a large cavity [8].

demonstrated that Raman spectroscopy is an effective tool in studying the nature of stored hydrogen molecules as well as in determining relative occupancy in different cavities [8].

4. Thermodynamic Prediction of Hydrates Containing THF and H₂

A thermodynamic model based on the CSMGem framework (an in-house program based on the van der Waals and Platteeuw theory) was developed for hydrate systems containing THF and H₂. With the newly developed model, thermodynamic predictions of many simple or binary hydrates containing THF or H₂ can be made for the first time. The model predictions are in excellent agreement with experimentally determined p-T phase diagrams. Such a model is very useful since THF is a common additive for reducing the formation pressure of a given hydrate system, and binary hydrates of hydrogen are currently being investigated as a potential storage material. The model also indicates that the degree to which the cavities are filled with hydrogen is largely a function of formation pressure, which has an implication in hydrogen storage, where high occupancy is desired [9].

Summary and Implications

The newly proven concept of chemical-clathrate hybrid storage of hydrogen holds great promise for improving the storage capacity in clathrate materials. Applying this concept to clathrate hydrates resulted in an increased storage capacity while having a large guest present, which greatly reduces the required formation pressure at a given temperature. Using spectroscopic tools, we have obtained new insight into the structure and interactions between the host water molecules and the guest hydrogen molecules in clathrate hydrates of

FIGURE 4. Pressure-temperature diagram of THF + H₂ hydrate experimentally determined by various groups (shown as dots) predicted by the newly developed thermodynamic model (shown as solid lines) [9].

hydrogen. We are continuing our efforts to develop new materials that can be used for efficient storage of hydrogen.

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IV.I.21 Mechanistic Studies of Activated Hydrogen Release from Amine Boranes

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Research Scope and Objectives

Effective storage of hydrogen presents one of the most significant technical gaps to successful implementation of the hydrogen economy, particularly for transportation applications. Amine boranes, such as ammonia borane H_3NBH_3 and ammonia triborane $\text{H}_3\text{NB}_3\text{H}_7$, have been identified as promising, high-capacity chemical hydrogen storage media containing potentially readily released protic (N-H) and hydridic (B-H) hydrogens. At the outset of our studies, dehydrogenation of ammonia borane had been studied primarily in the solid state, but our work carried out under the previous grant clearly demonstrated that ionic liquids, base-initiators and/or metal-catalysts can each significantly increase both the rate and extent of hydrogen release from amine boranes under moderate conditions. Our studies have also shown that depending upon the activation method, hydrogen release from amine boranes can occur by very different mechanistic pathways and yield different types of spent-fuel materials. The goal of the current project is to develop a fundamental understanding of each of these hydrogen-release mechanisms and to elucidate the important controlling factors for each type of reaction. Such detailed understanding is vital to the continued discovery and optimization of new chemical-hydride based hydrogen release systems.

Recent Progress

The high hydrogen release capacity that could potentially be achieved by ammonia triborane **1** oxidative-hydrolysis, (9.7 materials-wt% H_2) or thermolysis (17.7 materials-wt% H_2), has made it an attractive candidate for chemical hydrogen storage. Although $\text{NH}_3\text{B}_3\text{H}_7$ was first synthesized over 50 years ago, owing to the lack of a suitable method for its efficient and safe synthesis, its reactivities and properties have not been intensively explored. Of the fewer than 30 previous publications on **1**, many were stimulated by the apparent contradiction between the computational studies that predict a symmetric single hydrogen-bridged C_s -symmetric structure, and the early single crystal X-ray determination of **1** that showed an asymmetric structure with perhaps two bridging-hydrogens. In a recently published paper [1] we presented: (1) a new, efficient preparation of **1** that now makes this compound easily available; (2) a new crystallographic study of the solid-state structure of **1**, along with a structural determination of the **1**•18-crown-6 adduct, that resolves the contradictions with computational structural predictions; and (3) a description of the hydrolytic hydrogen release properties of **1**.

Iodine oxidation of B_3H_8^- in glyme solution to produce (glyme) B_3H_7 , followed by displacement of the coordinated glyme by reaction with anhydrous ammonia provides a safe and convenient preparation of ammonia triborane. X-ray crystallographic determinations and DFT computational studies of both $\text{NH}_3\text{B}_3\text{H}_7$ and the $\text{NH}_3\text{B}_3\text{H}_7$ •18-crown-6 adduct demonstrate that while computations predict a symmetric single bridging-hydrogen conformation, $\text{NH}_3\text{B}_3\text{H}_7$ has a highly asymmetric structure in the solid-state that results from intermolecular $\text{N-H}^+\cdots\text{H}^-\text{B}$ dihydrogen bonding interactions.

Studies of its hydrolytic reactions showed that upon the addition of acid or an appropriate transition metal catalyst, aqueous solutions of **1** rapidly release hydrogen, with the rate of H_2 -release controlled by both the catalyst loadings and temperature. The hydrolysis reaction of a highly concentrated 22.7 wt% sample yielded 6.1 materials-wt% H_2 making an ammonia triborane based hydrolytic system competitive with both NH_3BH_3 and NaBH_4 based hydrolysis systems. As will be discussed in future publications, the development of an efficient synthesis of **1** is now enabling systematic investigations of the chemistry and applications of this unique compound.

We have previously shown that ionic liquids provide advantageous media for ammonia borane

FIGURE 1. Left: Comparison of (a) the solid-state structure of **1** with (b) the DFT-optimized **1** structure. Dashed lines indicate the positions of the dihydrogen bonding interactions. Right: (top) X-ray crystal structure of **1**•18-crown-6 (molecule a); (bottom) selected distances in the ammonia triborane fragment of **1**•18-crown-6 (molecule a).

dehydrogenation in which both the extent and rate of dehydrogenation are significantly increased [2]. Furthermore, in contrast to the results found for solid-state reactions, when ammonia borane dehydrogenation was carried out in ionic liquids, no induction period was observed. Work in the last year [3] has focused on using both solid-state and ionic-liquid solution NMR studies to identify the mechanistic pathways and key intermediates involved in AB H₂-release in ionic-liquids. These studies have provided strong evidence for the mechanistic pathway illustrated in Figure 3 involving the initial ionic liquid promoted formation of the diammoniate of diborane (DADB) followed by the reaction of DADB with additional AB to produce saturated polyaminoborane polymers. At the outset of our studies, we thought that subsequent dehydrogenation of this polymer could occur along either of two main mechanistic pathways. As shown on the left, H₂-release could proceed by cyclization and chain-branching reactions, ultimately yielding saturated materials that preserve the sp³ framework. However, the NMR studies strongly favor instead the process on the right, involving H₂-elimination from adjacent polyaminoborane BH and NH groups to produce B=N unsaturated polyiminoboranes that furtherreact to form cross-linked sp²-bonded polyborazylene materials.

Other synthetic, mechanistic and computational studies conducted in the last year have also demonstrated that strong nitrogen bases, such as Proton

Sponge (1,8-bis(dimethylamino)naphthalene) [4], induce H₂-release from ammonia borane by a different mechanistic pathway involving the initial deprotonation of AB to produce the H₂NBH₃⁻ anion. This anion then induces anionic dehydropolymerization of additional ammonia borane to produce a growing polyaminoborane polymer with a resulting significant increase in the hydrogen release rate.

Previous work on metal-catalyzed dehydrogenation of ammonia borane (AB) indicated that some catalysts afforded aminoborane oligomers, (NH₂BH₂)_n, and one equivalent of H₂ whereas others gave borazine, (NHBH)₃, BN cross-linked borazine (polyborazylene, BNHx) and > 2 equiv. H₂. Post-catalysis characterization of soluble Ir⁵ and Ru⁶ complexes showed that both processes involve homogeneous catalysis and theoretical treatments proposed a variety of activation mechanisms [7-9]. Detailed in situ multinuclear NMR studies of substituted amine-boranes and external trapping studies using cyclohexene demonstrated that ejection of reactive aminoborane, NH₂BH₂ [10], from the metal center leads to rapid trapping by AB to afford the BN analog of ethylcyclobutane [B-(cycloborazanyl)amine borane, CDBAB, Scheme 1).

Conversion of CDBAB to borazine and subsequent cross-linking to polyborazylene affords more than 2 equiv. H₂ per AB (Scheme 2). In collaboration with

FIGURE 2. Ammonia-Borane H₂-Release Mechanism in Ionic Liquids

Heinz Berke (University of Zurich, Switzerland) we have now used reactive imines to prepare CDBAB in good yield (Equations 1 and 2).

Studies of the thermolysis and catalyzed dehydrogenation of CDBAB are in progress as are attempts to catalyze the cross-linking of borazine.

Inefficient ejection of aminoborane from the metal center leads to coordination complexes, $[M](NH_2BH_2)_2$, that limit the hydrogen released for AB to a single equivalent. Thus, cyclohexene trapping of NH_2BH_2 is not observed with $Cr(CO)_5(NMe_3)$ or the above-mentioned Ir complex catalyst. In collaboration with Jun Li and Don Camaioni (Pacific Northwest National Lab) we have now shown that the Cr catalyst effects AB dehydrogenation through a Lewis acid activation mechanism and the resulting aminoborane complex is predicted to exhibit a 90° Cr-NB angle (Figure 1A) due to the unusual sigma-backbonding interaction of a filled Cr d orbital with the empty p orbital on B (Figure 1B).

FIGURE 3. A) Electronic structure of Cr(CO)₅(NH₂BH₂) from DFT calculation (B3LYP/6311+G**); B) HOMO-1 orbital depicting sigma back-bonding interaction.

We have now isolated the first aminoborane coordination complexes, [M](NH₂BH₂), with M = Cr(CO)₅ and [Mn(CO)₅]⁺ and are investigating their reactivity with additional AB to test our proposed dehydrocyclization pathway (Scheme 3) to give cyclopentaborazane, (NH₂BH₂)₅. Confirmation of the structure of this pentamer using variable field, variable temperature solidstate NMR is in progress and we are also trying to co-crystallize the compound with crown ethers.

Future studies include detailed mechanistic studies of the reactions and interactions of amine-boranes, including ammonia borane, the diammoniate of diborane, [(NH₃)₂BH₂⁺][BH₄⁻] and ammonia triborane NH₃B₃H₇, with a range of potential dehydrogenation promoters and/or catalysts. Computational and experimental studies involve kinetic measurements, isotope labeling studies and the quantification of H₂-release, along with product characterizations by ¹¹B NMR and DFT/GIAO calculations and mass spectral analyses of both the solid and volatile dehydrogenation products. In situ monitoring of reactions by ¹¹B NMR in room temperature ionic liquids are again being used for direct observation of any differences in mechanistic steps and intermediates. Having identified disparate mechanisms for hydrogen release from AB using ionic liquids (cationic or anionic oligomerization) and metal catalysts (formation of reactive aminoborane), much of our future work will focus on metal catalysis in ionic liquids in order to develop catalysts that are effective for releasing more than two equivalents of hydrogen per AB.

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IV.I.22 Computational Studies of Hydrogen Interactions with Storage Materials

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Brief Description of Accomplishments

During our second year we have continued to make substantial progress in all areas of the project: interstitial hydrogen in metals, diffusion in metal hydrides, and kinetics of complex hydrides. The overall goal is to elucidate the physics and chemistry of hydrogen interactions with hydrogen storage materials by performing first-principles calculations based on density functional theory (DFT). By specifically addressing the behavior of hydrogen-related and other point defects, we are able to investigate the kinetics of hydrogen uptake and release, the decomposition of complex hydrides, and the effect of adding impurities to the system. Our approach takes into account that defects and impurities in non-metallic systems can occur in charge states other than the neutral state; this important aspect of the problem had not been addressed in previous computational studies performed to date, and our investigations show that it has extremely important consequences for defect concentration and diffusion. Other groups are now starting to apply the same methodology.

Structural optimization, total energy and electronic structure calculations are performed based on DFT using the generalized-gradient approximation (GGA) and the projector-augmented wave (PAW) method as implemented in the VASP code.

Below, we briefly summarize results in each of the main topical areas of the project.

1. Metals: Hydrogen and Vacancies in Al and Mg

Al-based and Mg-based hydrides have great potential as reversible hydrogen storage materials. It is essential to understand the structure and stability of hydrogen as an impurity in the bulk of these materials. Recent theoretical [1,2] and experimental studies [3] indicate that trapping of H at vacancies in Al significantly slows down the diffusion through

the crystal. It has been also suggested that multiple H atoms might be trapped in an Al vacancy, which overcompensates the energy cost to form the defect and could induce superabundant vacancy concentrations and vacancy clustering [4]; this process could potentially play an important role in hydride formation. In the case of Mg, much less is known about H as an impurity and the H-vacancy interaction; a recently published experimental study reports that H have much lower formation energies than vacancies in Mg [5].

The differences between Al and Mg motivated us to investigate and compare the properties of H impurities in Al and Mg. Our calculations build on investigations of isolated interstitial hydrogen, interstitial H_2 molecules, and isolated vacancies in the material. We find that in both materials individual vacancies can in principle host up to two or eight H atoms, not 12 as previously reported [2,4]. The character of the H-vacancy interaction strongly depends on the amount of hydrogen dissolved in the metal, which in turn is determined by the hydrogen chemical potential. We evaluate the concentrations of the relevant hydrogen-vacancy complexes as a function of hydrogen chemical potential, ranging from normal conditions over high pressures to hydrogen plasma. Our analysis reveals fundamental differences between the characteristics of the H-vacancy interaction in Al and Mg: Al shows significant H trapping for low as well as for very high hydrogen chemical potentials, while Mg shows H trapping only at high chemical potentials. However, in Mg a moderate pressure increase of H_2 gas (on the order of 1 GPa at room temperature) is sufficient to induce H-enhanced superabundant vacancy formation, which in Al is possible only at very high hydrogen chemical potentials (as for example obtained with a hydrogen plasma).

2. Metal Hydrides: Point Defects in MgH_2

We are focusing on MgH_2 , a material that is not a suitable storage material in its own right because of unfavorable kinetics. However, it is a constituent of other compound materials that are currently being investigated, and we also feel it can provide useful insights in the fundamental mechanisms of hydrogen kinetics in hydrides.

We have investigated the possible native point defects in bulk MgH_2 . We find that under H-poor conditions the lowest energy defects are positively and negatively charged vacancies (V_H^+ and V_H^-). Under H-rich conditions, the lowest energy defects are V_H^+ , H_i^- , and V_{Mg}^{2-} . We have also calculated interstitial H_2 , which is stable mainly in the neutral charge state, and Mg

interstitials, which are higher in energy than the other point defects. The behavior of V_{Mg} is unusual in that it is amphoteric, i.e., it can act either as a donor or an acceptor. Cation vacancies in ionic materials usually act exclusively as acceptors.

The defects are characterized by unusually large local structural rearrangements, which strongly depend on the charge state of the defect. The hydrogen-related defects are also highly mobile, with migration barriers on the order of 0.1 eV or less for H_i^+ , H_i^- and H_{2i} . Vacancies have somewhat higher migration barriers: 0.38 eV for V_{H}^+ and 0.63 eV for V_{H}^- . The migration barrier for V_{Mg}^{2-} is 0.74 eV. By combining the calculated formation energies with migration barriers, we can estimate activation energies for hydrogen self-diffusion, finding a value of 1.48 eV for V_{H}^+ -mediated diffusion under conditions corresponding to hydrogen desorption; this value falls within the experimentally reported range [6].

3. Complex Hydrides: Alanates

In the area of complex hydrides, we have expanded our studies beyond NaAlH_4 to materials such as LiBH_4 , Li_2NH , and LiNH_2 . In addition, we are investigating not just hydrogen-related but also other point defects, with the goal of elucidating decomposition reactions. We have also performed investigations of various transition-metal additives and their effects on diffusion.

3.a. NaAlH_4

In addition to the studies of hydrogen-related point defects that were previously reported [7], we have performed detailed investigations of the atomic structure of the point defects [8] and compared the results with muon spin rotation experiments [9]. We have also completed a comprehensive study of Na- and Al-related defects in NaAlH_4 . Our analysis indicates that the structure and energetics of these defects can be interpreted in terms of elementary building blocks, which include $V_{\text{AlH}_4}^+$, V_{Na}^- , V_{H}^+ , H_i^- , and H_{2i} . Other point defects, such as V_{Al} , Al_i , and Na_i are found to be less important.

We have calculated formation energies as well as migration barriers for the key defects, in order to compare diffusion activation energies to experimentally measured activation energies of desorption. Our results exhibit some key differences from previous studies [10,11]. As previously reported, migration barriers for hydrogen-related defects are very low. For $V_{\text{AlH}_4}^+$ we find a barrier of 0.46 eV; for V_{Na}^- , 0.41 eV. Based on our calculated numbers, we conclude it is highly unlikely that neutral V_{AlH_3} or V_{NaH} entities would play a role. We argue that $V_{\text{AlH}_4}^+$ and/or V_{Na}^- are the key defects responsible for Al and Na transport. Each of these will not occur on its own, but in combination with one or more hydrogen-related defects; in particular, H_i^- and

V_{H}^+ act as charge-carrying defects that will provide the necessary local charge neutrality. The resulting activation energies are in agreement with experimental observations [12].

Finally, we have completed our study of fluorine and chlorine interactions with NaAlH_4 [13], motivated by the fact that TiF_3 and TiCl_3 are frequently used to introduce Ti into NaAlH_4 . Fluorine substitution for hydrogen has been proposed as a means of destabilizing hydrides, but we find this to be unlikely for either NaAlH_4 or Na_3AlH_6 . Fluorine interstitials are most stable as charged defects; however, their concentration will likely be too low to affect the electronic structure or diffusion of point defects. The migration barrier for interstitial fluorine is low enough to easily allow diffusion during cycling through the hydride phases. Chlorine has a large size mismatch with hydrogen and every chlorine-related defect studied was found to have a high formation energy. Chlorine is therefore unlikely to incorporate in NaAlH_4 .

3.b. LiBH_4

Our calculated atomic and electronic structure of bulk LiBH_4 (space group *Prima*, 24 atoms/unit cell) is in agreement with previous reports [14,15]. The calculated GGA band gap of LiBH_4 is 7.01 eV; the valence-band maximum (VBM) is dominated by bonding states consisting of B *p* and H *s* states, whereas the conduction-band minimum (CBM) consists predominantly of the anti-bonding state of B *p* and H *s* states plus contributions from Li *s* states. The decomposition process in LiBH_4 can proceed as $\text{LiBH}_4 \rightarrow \text{LiH} + \text{B} + 3/2 \text{H}_2$. We therefore assume that the chemical potentials of Li, B, and H can be obtained from the equations that express the stability of LiH, B, and LiBH_4 . The lowest-energy hydrogen-related defects are V_{H}^+ and H_i^- .

We have investigated the atomic and electronic structure of various transition metal impurities in LiBH_4 . Some of the impurities induce a substantial shift in the Fermi level, relative to the value in undoped material. Such a shift will lower the formation energy of charged point defects and thereby enhance the kinetics, as proposed in Ref. [7]. Based on this analysis we are able to identify impurities that would be most effective in enhancing kinetics.

3.c. LiNH_2 and Li_2NH

Bulk LiNH_2 has a tetragonal space group $I\bar{4}$ and 32 atoms/unit cell) [16]; our calculated lattice parameters and formation enthalpy (-2.065 eV/f.u.) are in qualitative agreement with previous work [16-19]. Our new results include an examination of the band structure and density of states. The VBM of LiNH_2 consists predominantly of N *p* states, with some contribution from Li *s* and H *s* states; the CBM consists

predominantly of N *p* states and some contribution from Li *s* states. The calculated DFT-GGA band gap is 3.17 eV; the band gap is indirect with the VBM at the M point and the CBM at the Γ point. For bulk Li_2NH we assume a hypothetical orthorhombic phase with space group *Pbca* and 32 atoms/unit cell [20]. Again, calculated structural properties are in good agreement with previous work [20]. The calculated DFT-GGA band gap is direct, with a value of 2.26 eV.

It was observed by Chen *et al.* [21] that a mixture of LiNH_2 and Li_2NH released hydrogen via a two-step reaction: $\text{LiNH}_2 + 2 \text{LiH} \leftrightarrow \text{Li}_2\text{NH} + \text{LiH} + \text{H}_2 \leftrightarrow \text{Li}_3\text{N} + 2\text{H}_2$. We therefore assume that LiNH_2 is in equilibrium with Li_2NH and LiH , and the chemical potentials of Li, N, and H in LiNH_2 can then be obtained from the equations that express the stability of Li_2NH , LiH , and LiNH_2 . Similarly, the chemical potentials of Li, N, and H in Li_2NH can be obtained by assuming equilibrium with LiH and Li_3N .

For LiNH_2 , we find that the dominant H-related defects are H_i^+ and V_H^- . The Fermi-level position where these two defects have equal formation energies is ~ 2.2 eV. H_i^+ corresponds to the formation on an NH_3 unit. We have also examined Li and NH_2 -related point defects, finding $\text{V}_{\text{NH}_2}^+$ and V_{Li}^- to be the lowest-energy ones. The results are qualitatively similar in Li_2NH ; now the Fermi-level position where H_i^+ and V_H^- have equal formation energies is at ~ 1.4 eV. The alignment between hydrogen-related levels in the two materials is consistent if we assume a valence-band offset of ~ 0.9 eV in going from LiNH_2 to Li_2NH . In Li_2NH , $\text{V}_{\text{NH}_2}^{2+}$ is lower in energy than $\text{V}_{\text{NH}_2}^+$ for relevant positions of the Fermi level. All of these defects are instrumental in diffusion of H, Li, and N.

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1. "Formation and migration of charged native point defects in MgH_2 : First-principles calculations, M. S. Park, A. Janotti, and C. G. Van de Walle (Phys. Rev. B).
2. "Hydrogen interactions with vacancies in Al and Mg: A comparative analysis based on density functional theory", M. S. Park, L. Ismer, A. Janotti, and C. G. Van de Walle (Phys. Rev. B).
3. "Formation and migration of native defects in NaAlH_4 ", G. B. Wilson-Short, A. Janotti, K. Hoang, and C. G. Van de Walle (Phys. Rev. B).

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IV.I.23 Quantum Tuning of Chemical Reactivity for Storage and Generation of Hydrogen

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General Overview

This work is a joint experimental and theoretical study that focuses on establishing the fundamental underpinnings for chemical adsorption, dissociation, absorption, diffusion, and recombination of gaseous species on *quantum-mechanically confined thin films and alloys of light* metal elements with specific emphasis on hydrogen. Fundamental understanding of these quantum phenomena, including the quantum stabilization of thermodynamically immiscible alloy species and their potential for tuning surface catalytic processes, are directly relevant to the use of light-metal hydrides as storage media for hydrogen. Potential conceptual advances in this research area may also have a broader impact in gaining better understanding of the microscopic origin of catalysis, and in designing new types of catalysts for alternative energy and environmental applications.

During the first phase of the project, our experimental effort is primarily focused on growing atomically smooth ultrathin magnesium films on Mo(110) and Si(111) substrates and the investigation of quantum size effects on plasmon excitations and hydrogen adsorption. Theoretical efforts within first-principles approaches have been made in order to understand the fundamental properties of pure and alloyed Mg films and their interactions with hydrogen.

We have also carried out a combined experimental and theoretical study of the formation of surface alloys at the top of ultrathin metal layers of varying thicknesses grown in the quantum regime, and explored the corresponding changes in the surface activity as measured by the oxidation rates.

A parallel effort is undertaken to investigate the role of Friedel oscillations in the quantum stability of ultrathin films and the solubility of a second metal element, using Pb as a model system. Such *fundamental* understanding may lead to the creation of novel

metastable alloys with vastly improved properties for hydrogen storage or other applications such as plasmonics or superconductivity.

Thin Film Growth

Low temperature growth of Mg on Mo(110) and Si(111) substrates results in the formation of atomically smooth thin films with precisely controlled film thickness, as indicated by scanning tunneling microscopy and Auger electron spectroscopy data. Depending on the growth temperature, Mg growth on Si(111) is preceded by the formation of an ultrathin silicide layer. On both substrates, Mg films grow in the hexagonal close packed (0001) orientation and the existence of discrete quantum well states was inferred from scanning tunneling spectroscopy data as a function of the film thickness.

On the theory side, we have investigated structural stabilities of $\text{Mg}_{1-x}\text{Al}_x$ and $\text{Mg}_{1-x}\text{Na}_x$ thin films and found that their formation energy as well as the Fermi energy and work function vary strongly with thickness. These effects seem to be closely related to quantum confinement effects. We have also carried out a more comprehensive model study of the quantum stability of metal films under various conditions and on different substrates, aimed to offer a critical assessment of the various factors contributing to the quantum stability.

Quantized Plasmons

X-ray photoemission (XPS) experiments yielded compelling evidence for the importance of size quantization of the electronic properties, specifically the plasmons. Using XPS, we monitored the evolution of a sharp shake-up satellite in the Mg 1s core level as a function of the film thickness. For films with thicknesses between five and twenty five atomic layers the energy position of this peak is inversely proportional to the square of the film thickness. These results are consistent with the existence of *quantized* plasmons, which we interpret on the basis of theoretical (hydrodynamics and random-phase approximation) descriptions of the density-response function. We demonstrated that the observed loss feature corresponds to the $n = 1$ *antisymmetric* (i.e., third) normal mode of the thin film, consistent with the fact that in the ultrathin film limit the symmetric plasmons have vanishing spectral weight—a striking manifestation of the role of size quantization on plasmon resonances in precisely controlled nanostructures.

The role of size quantization is also evident from the evolution of the plasmon loss intensity. We found that the plasmon creation probability after photoionization (i.e., extrinsic plasmon excitation) decreases with decreasing film thickness. This is qualitatively consistent with the notion that for a given quantum number (i.e., $n = 1$ *antisymmetric*), the perpendicular wave vector increases as the film thickness decreases, which in turn should lead to increased Landau damping of the volume plasmon and a reduction of the loss intensity. The observation of size quantization of plasmon modes adds an interesting new flavor to the concept of nanoplasmonics, including the possibility of tuning surface photochemical reactions via the plasmon resonance and its coupling to electromagnetic wave fields.

Hydrogen Adsorption

We constructed a new system for temperature-programmed desorption (TPD) and succeeded in producing highly linear temperature ramps. Preliminary investigations of Mg desorption suggest rather complex line shapes for multilayer desorption, which are currently being analyzed. Atomically smooth Mg films with thicknesses ranging from 5 to 25 atomic layers have been exposed to atomic deuterium and their TPD spectra have been measured as a function of film thickness. The peak temperature for deuterium desorption varies from 463 K to 505 K, depending on the film thickness. We are currently exploring whether the variation can be attributed to quantum size effects. A complicating factor is the stability of the Mg film itself which desorbs at slightly higher temperature (539 K). The TPD data are currently being complemented with nuclear reaction analysis, scanning tunneling microscopy, and electron energy loss spectroscopy.

Theoretically, we find that the interaction of hydrogen with Mg thin films and thin film alloys is highly tunable. Structural properties such as the lattice spacing can be varied by several percents via alloying, whereas the work function can be tuned over a few tenths of an electron volt. The combined effects of alloying and lattice strain produce a very rich parameter space for tuning hydrogen binding energies. For example, we found that by applying strain of $\pm 5\%$, the work function changes by 0.6 eV and the H-binding strength changes by as much as 0.3 eV per hydrogen atom for a given film thickness. These fundamental findings open up new possibilities of using Mg films for realistic H-storage materials.

Surface Alloying of Quantum Metal Films for Enhanced Chemical Reactivity

Using scanning tunneling microscopy and spectroscopy, we have demonstrated that the adsorption

of a minute amount of Cs on a Pb mesa grown in the quantum regime can induce dramatic morphological changes of the mesa, characterized by the appearance of populous monatomic-layer-high Pb islands on top of the mesa. The edges of the Pb islands are decorated with Cs adatoms, and the islands preferentially nucleate and grow on the quantum mechanically unstable regions of the mesa. Furthermore, first-principles calculations within density functional theory have shown that the Pb atoms forming the islands were expelled by the adsorbed Cs atoms via a kinetically accessible concerted place exchange process as the Cs atoms alloy into the top layer of the Pb mesa. These findings have important implications in quantum design of new types of catalysts via surface alloying, as illustrated by the greatly enhanced oxidation rates on the Cs-alloyed Pb films.

Friedel Oscillations, Stability, and Kinetic Solubility

Because the quantum size effect is the key parameter for controlling the structure, morphology, and chemical reactivity of ultrathin metal film, we continue our line of research aimed at elucidating the origins of strong quantum size effects in Pb(111) which has been the model system of quantum-size-effect physics. Using first-principles density functional theory, we calculated the relaxations of the interlayer spacing in Pb(111) films. We find that both the sign and magnitude of the lattice relaxations oscillate with the distance x from the surface, and persist into the films with a $1/x$ decay law. The interference of such persistent oscillations, in turn, can result in unusually large lattice relaxations at the center of the films, and the overall driving force is attributed to the Friedel oscillations in electron density, which also decays with a $1/x$ power law. In contrast, for Pb(110), Pb(100), and Al(111) films, both the Friedel oscillations and interlayer relaxations decay with the standard $1/x^2$ power law. One important conclusion is that the unusually slow decay of the Friedel oscillations in Pb(111) implies that the perturbation of the electron gas at one of the confining boundaries is felt by the other boundary of the film even if these boundaries are far apart, which explains why quantum size effects in Pb(111) films are so exceptionally robust. An intriguing question that remains to be answered is whether the $1/x$ decay in Friedel oscillations could be attributed to Fermi surface nesting along the Pb [111] direction. This in turn would suggest that bulk alloys with nested Fermi surfaces would be good candidates for the exploration of quantum size effect physics.

A parallel experimental effort is aimed at tuning the thermodynamic solubility of metal alloys via the quantum size effect, using $Pb_{1-x}Ga_x$ as a prototypical alloy system for showing exceptionally strong quantum size effects in the nanoscale regime and zero miscibility in the bulk limit. The underlying idea is that alloying provides an independent means of tuning the electronic

structure and surface chemical reactivity of quantum confined crystalline thin films. We find that atomically smooth ultrathin films of $\text{Pb}_{1-x}\text{Ga}_x$ alloy ($x=0.06$) can be stabilized on a Si(111)7x7 substrate through the quantum size effect. The superconductive properties of these films clearly indicate that Pb and Ga do alloy in the ultrathin film regime. Quantum stabilized growth defects, consisting of deep holes extending to the film-substrate interface, act as pinning centers for vortices in the superconducting state. The present study highlights the possibility of growing new alloys beyond the solid solubility limit and controlling critical state properties in the quantum regime.

List of Papers

1. **Quantized Plasmons in Ultrathin Magnesium Films**, M.M. Özer, A.G. Eguiluz, and H.H. Weitering, *Phys. Rev. Lett.*, submitted.
2. **“Particle in a Box” Experiments in the Laboratory: Quantum Size Effects on Growth, Superconductivity, and Plasmon Excitations of Ultra-Thin Metal Films**, M.M. Özer, and H.H. Weitering, *J. Low Temp. Phys.*, submitted.
3. **Persistent oscillations in the interlayer lattice relaxation of Pb(111) films**, Y. Jia, B. Wu, T.L. Einstein, H.H. Weitering, and Z.Y. Zhang, *Phys. Rev. Lett.*, submitted.
4. **Magnetic doping of group IV semiconductors**, M.M. Özer, C.G. Zeng and H.H. Weitering, Invited Book Chapter in “Spintronic Semiconductors”, edited by Weimin M. Chen and Irina Buyanovaw, Pan Stanford Publishing, 2009 (in print).

5. **Surface Alloying and Morphological Restructuring of Quantum Metal Films for Enhanced Chemical Reactivity**, Alexander Khajetoorians, Wenguang Zhu, Jisun Kim, Shengyong Qin, Holger Eisele, Zhenyu Zhang, and Chih-Kang Shih, *Proc. National Academy of Sci.* submitted.
6. **Interaction between Dihydrogen and Metallofullerenes**, M. Yoon, S. Yang, and Z.Y. Zhang, *J. Chem. Phys.*, submitted.
7. **Stability of metallic thin film with free electron model**, B. Wu and Z.Y. Zhang, *Phys. Rev. B* 77, 035410 (2008).
8. **Calcium as the Superior Coating Metal in Functionalization of Carbon Fullerenes for High-Capacity Hydrogen Storage**, M. Yoon, S.Y. Yang, C. Hicke, E.G. Wang, D. Geohegan, and Z.Y. Zhang, *Phys. Rev. Lett.* 100, 206806 (2008).

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IV.I.24 From Fundamental Understanding to Predicting New Nanomaterials for High-Capacity Hydrogen Storage

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Project Scope

The main scope of this BES proposal is to focus on achieving fundamental understanding of the chemical and structural interactions governing the storage and release of hydrogen in a wide spectrum of candidate materials. The goals are:

- To provide fundamental understanding of how the most of the candidate materials (MOFs, alanates, destabilized chemical hydrides, etc) interact with H₂ chemically, structurally and energetically; and
- To provide timely feedback and guidance from theory to de novo materials design and targeted syntheses throughout the DOE programs.

Below we present a brief summary of the selected twelve papers which have already been published during 2008-April 2009. The first six of these are resulted from the initial phase of our project which was funded as an add-on DOE BES proposal to Prof. Jack's Fischer's existing grant "Carbon Nanotubes: Properties and Applications" (DE-FG02-98ER45701). In the last six publications, we acknowledge the new grant number, DOE-BES-08ER46522, which has been started on 8-15-2008. At the end of the report, we give the total list of publications and people working on the project.

Research Accomplishments

1. Functionalization of Carbon-Based Nanostructures with Light Transition-Metal Atoms for Hydrogen Storage, E. Durgun, S. Ciraci, and T. Yildirim, *Phys. Rev. B*, **77**, 085405 (2008).

In this work, we extend our previous study further to investigate the hydrogen uptake by light transition-metal atoms decorating various carbon-based nanostructures in different types of geometry and

dimensionality, such as carbon linear chain, graphene, and nanotubes. Using first-principles plane-wave method we show that not only outer but also inner surface of a large carbon nanotube can be utilized to bind more transition-metal atoms and hence to increase the storage capacity. We also found that scandium and vanadium atoms adsorbed on a carbon nanotube can bind up to five hydrogen molecules. Similarly, light transition-metal atoms can be adsorbed on both sides of graphene and each adsorbate can hold up to four hydrogen molecules yielding again a high-storage capacity. Interestingly, our results suggest that graphene can be considered as a potential high-capacity H₂ storage medium. We also performed transition state analysis on the possible dimerization of Ti atoms adsorbed on the graphene and single-wall carbon nanotube.

2. Metal-Organic Framework from an Anthracene Derivative Containing Nanoscopic Cages Exhibiting High Methane Uptake, Shengqian Ma, Daofeng Sun, Jason M. Simmons, Christopher D. Collier, Daqiang Yuan, and Hong-Cai Zhou, *J. Am. Chem. Soc.* **130**, 1012 (2008).

A microporous metal-organic framework, PCN-14, based on an anthracene derivative, 5,5'-(9,10-anthracenediyl)di-isophthalate (H₄adip), was synthesized under solvothermal reaction conditions. X-ray single crystal analysis revealed that PCN-14 consists of nanoscopic cages suitable for gas storage. N₂-

Different views of PCN-14, which exhibits record high methane absorption at room temperature.

adsorption studies of PCN-14 at 77 K reveal a Langmuir surface area of 2,176 m²/g and a pore volume of 0.87 cm³/g. Methane adsorption studies at 290 K and 35 bar show that PCN-14 exhibits an absolute methane-adsorption capacity of 230 v/v, 28% higher than the DOE target (180v/v) for methane storage.

3. Metal-Organic Frameworks Based on Double-Bond-Coupled Di-Isophthalate Linkers with High Hydrogen and Methane Uptakes, Xi-Sen Wang, Shengqian Ma, Karsten Rauch, Jason M. Simmons, Daqiang Yuan, Xiaoping Wang, Taner Yildirim, William C. Cole, Joseph J. López, Armin de Meijere, and Hong-Cai Zhou, *Chem. Mater.* **20**, 3145 (2008).

Utilization of double-bond-coupled di-isophthalate ligands, H₄aobtc and H₄sbtc, in reactions with Cu(NO₃)₂ yielded two isostructural microporous MOFs, PCN-10 and PCN-11, respectively. Upon guest removal, both MOFs contain two types of pores, open metal sites, and retain enduring porosity. In particular, both contain nanoscopic cages that are particularly suitable for gas storage. At 760 Torr, 77 K, the excess hydrogen uptake of PCN-10 is 2.34 wt% (18.0 g/L) and that of PCN-11 is as high as 2.55 wt% (19.1 g/L). Gas adsorption experiments suggest that MOFs containing CdC double bonds are more favorable than those with NdN double bond in retaining enduring porosity after thermal activation, although the NdN double bond has slightly higher H₂ affinity. When the pressure is increased, the excess adsorption at 77 K saturates around 20 atm and reaches values of 4.33% (33.2 g/L) and 5.05% (37.8 g/L) for PCN-10 and PCN-11, respectively. In addition, PCN-11 exhibits an excess methane uptake of 171 cm³(STP)/cm³ at 298 K and 35 bar, approaching the DOE target of 180 v(STP)/v for methane storage at ambient temperatures. Thus, PCN-11 represents one of the few materials that are applicable to both hydrogen and methane storage applications.

4. Origin of the Exceptional Negative Thermal Expansion in Metal-Organic Framework-5, Wei Zhou, Hui Wu, and Taner Yildirim, J.R. Simpson and A.R. Hight Walker, *Phys. Rev. B*, **78**, 054114 (2008).

Metal-organic framework-5 possesses an exceptionally large negative thermal-expansion (NTE)

coefficient. Our direct experimental measurement, in the temperature range of 4 to 600 K, shows that the linear thermal-expansion coefficient is $\sim -16 \times 10^{-6} \text{ K}^{-1}$. From first-principles lattice dynamics calculations, we deciphered the origin of this large NTE behavior. We found that almost all low-frequency lattice vibrational modes (below $\sim 23 \text{ meV}$) involve the motion of the benzene rings and the ZnO₄ tetrahedra as rigid units and the carboxyl groups as bridges. These rigid-unit modes exhibit various degrees of phonon softening and thus are directly responsible for the large negative thermal expansion in MOF-5.

5. Nature and Tunability of Enhanced Hydrogen Binding in Metal-Organic Frameworks with Exposed Transition Metal Sites Wei Zhou and Taner Yildirim, *J. Am. Chem. Soc.* **112**, 8132 (2008).

Metal-organic framework (MOF) compounds with exposed transition-metal (TM) sites were recently found to exhibit significantly larger experimental heats of adsorption of H₂ than classical MOFs, thus attracting greater attention. Here we show that the hydrogen binding in Mn₄Cl-MOF is not of the expected Kubas type because there is (a) no significant charge transfer from TM to H₂, (b) no evidence of any H₂-σ* Mn-d orbital hybridization, (c) no significant H-H bond elongation, and (d) no significant shift in H-H stretching mode frequency. We make predictions for the magnetic superexchange interactions in Mn₄Cl-MOF and determined low- and high-spin states of the Mn ion as local minima with very different hydrogen binding energies. We show that, by replacing Cl with F or Br, one can tune the H₂ binding energy. We further

Contour plot of the orientation dependence of the binding energy of H₂ on Mn₄Cl-MOF cluster in (θ, φ) space. The red and blue regions represent strong and weak binding energies, respectively.

reveal that the major contribution to the overall binding comes from the classical Coulomb interaction which is not screened due to the open-metal site and explains the relatively high binding energies and short H_2 -TM distances observed in MOFs with exposed metal sites compared to traditional ones. Finally, we show that the orientation of H_2 has a surprisingly large effect on the binding potential, reducing the classical binding energy by almost 30%.

6. Quasi-Free Methyl Rotation in Zeolitic Imidazolate Framework-8, W. Zhou, H. Wu, T.J. Udovic, J.J. Rush, and Taner Yildirim, *J. Phys. Chem. A*, **112**, 12602 (2008).

The reorientational motion of the methyl group is an intriguing physics phenomenon. It can be well described by classical random jumps at high temperature, whereas at low temperature it is dominated by quantum-mechanical rotational tunneling. Using neutron inelastic scattering and diffraction, we have studied the quantum methyl rotation in ZIF-8. The rotational potential for the CH_3 groups in ZIF-8 is shown to be primarily 3-fold in character. The ground-state tunneling transitions at 1.4 K of 334 ± 1 μ eV for CH_3 groups in hydrogenated ZIF-8 and 33 ± 1 μ eV for CD_3 groups in deuterated ZIF-8 indicate that the barrier to internal rotation is small compared to almost all methylated compounds in the solid state and that methyl-methyl coupling is negligible.

7. Alkali and Alkaline-Earth Metal Amidoboranes: Structure, Crystal Chemistry, and Hydrogen Storage Properties, Hui Wu, Wei Zhou and Taner Yildirim, *J. Am. Chem. Soc.*, **130**, 14834 (2008).

Alkali- and alkaline-earth metal amidoboranes, a new class of compounds with rarely observed $[NH_2BH_3]^-$ units, have been recently reported to significantly improve the dehydrogenation properties of ammonia borane. We successfully prepared solvent-

free lithium amidoborane $LiNH_2BH_3$ and calcium amidoborane $Ca(NH_2BH_3)_2$, and for the first time determined their structures, using a combined X-ray diffraction and first-principles molecular dynamics simulated annealing method. Through detailed structural analysis and first-principles electronic structure calculations, the improved dehydrogenation properties are attributed to the different bonding nature and reactivity of the metal amidoboranes compared to NH_3BH_3 .

8. Enhanced H_2 Adsorption in Isostructural Metal-Organic Frameworks with Open Metal Sites: Strong Dependence of the Binding Strength on Metal Ions, Wei Zhou, Hui Wu, and Taner Yildirim, *J. Am. Chem. Soc.* **130**, 15268 (10/25/2008).

MOFs with open metal sites exhibit much stronger H_2 binding strength than classical MOFs. Yet, how the binding strength varies with different open metal species was previously unknown. We conducted a systematic study of the H_2 adsorption on a series of isostructural MOFs, $M_2(dhtp)$ ($M=Mg, Mn, Co, Ni, Zn$). The experimental Q_{st} for H_2 of these MOFs range from 8.5 to 12.9 KJ/mol, with increasing Q_{st} in the following order: Zn, Mn, Mg, Co, and Ni. The H_2 binding energies derived from DFT calculations follow the same trend. We also found a strong correlation between the metal ion radius, the M- H_2 distance and the H_2 binding strength, which provides a viable, empirical method to predict the relative H_2 binding strength of different open metals.

The c-axis view of the unit cell of MOF-74, showing the one-dimensional pore geometry.

Methane absorbed in MOF-74 as obtained from neutron diffraction.

9. High-Capacity Methane Storage in Metal-Organic Frameworks $M_2(\text{dhtp})$: The Important Role of Open Metal Sites, Hui Wu, Wei Zhou, and Taner Yildirim, *J. Am. Chem. Soc.* **131**, 4995 (03/10/2009).

We found that metal-organic framework (MOF) compounds $M_2(\text{dhtp})$ (open metal $M=\text{Mg, Mn, Co, Ni, Zn}$) possess exceptionally large densities of open metal sites. By adsorbing one CH_4 molecule per open metal, these sites alone can generate very large methane storage capacities, 160–174 $\text{cm}^3(\text{STP})/\text{cm}^3$, approaching the DOE target of 180 $\text{cm}^3(\text{STP})/\text{cm}^3$ for material-based methane storage at room temperature. Our adsorption isotherm measurements at 298 K and 35 bar for the five $M_2(\text{dhtp})$ compounds yield excess methane adsorption capacities ranging from 149 to 190 $\text{cm}^3(\text{STP})/\text{cm}^3$ (derived using their crystal densities), indeed roughly equal to the predicted, maximal adsorption capacities of the open metals (within 10%) in these MOFs. Among the five isostructural MOFs studied, $\text{Ni}_2(\text{dhtp})$ exhibits the highest methane storage capacity, $\sim 200 \text{ cm}^3(\text{STP})/\text{cm}^3$ in terms of absolute adsorption, potentially surpassing the DOE target by $\sim 10\%$. Our neutron diffraction experiments clearly reveal that the primary CH_4 adsorption occurs directly on the open metal sites. Initial first-principles calculations show that the binding energies of CH_4 on the open metal sites are significantly higher than those on typical adsorption sites in classical MOFs, consistent with the measured large heats of methane adsorption for these materials. We attribute the enhancement of the binding strength to the unscreened electrostatic interaction between CH_4 and the coordinatively unsaturated metal ions.

10. Methane Sorption in Nanoporous Metal-Organic Frameworks and First-Order Phase Transition of Confined Methane, Hui Wu, Wei Zhou and Taner Yildirim, *J. Phys. Chem. C*, **113**, 3029 (2009).

Using neutron powder diffraction, we have directly determined the methane sorption sites in two prototypical MOF materials: ZIF-8 and MOF-5. The primary methane adsorption sites are associated with the organic linkers in ZIF-8 and the metal oxide clusters in MOF-5. Methane molecules on these primary sites possess well-defined orientations, implying relatively

Methane adsorption sites in ZIF-8 and MOF-5 as revealed by neutron diffraction.

strong binding with the framework. With higher methane loading, extra methane molecules populate the secondary sites and are confined in the framework. The confined methanes are orientationally disordered and stabilized by the intermolecular interactions. An unusual reversible methane-induced structural phase transition in MOF host lattice is observed at $\sim 60 \text{ K}$ in both ZIF-8 and MOF-5 due to strong intermolecular interaction between confined methane molecules in the pores of the host lattice.

11. Hydrogen Adsorption in HKUST-1: a Combined Inelastic Neutron Scattering and First-Principles Study, Craig M Brown, Yun Liu, Taner Yildirim, Vanessa K. Peterson, and Cameron J Kepert, *Nanotechnology* **20**, 204025 (2009).

In this paper, we present combined inelastic neutron scattering measurements and detailed first-principles calculations aimed at unraveling the nature of hydrogen adsorption in HKUST-1, a metal-organic framework with unsaturated metal centers. We reveal that, in this system, the major contribution to the overall binding comes from the classical Coulomb interaction which is not screened due to the open metal site; this explains the relatively high binding energies and short H_2 -metal distances observed in MOFs with exposed metal sites as compared to traditional ones. Despite the short

Orientalional potential of hydrogen molecule absorbed in HKUST-1, indicating quasi-two dimensional potential.

distances, there is no indication of an elongation of the H–H bond for the bound H_2 molecule at the metal site. We find that both the phonon and rotational energy levels of the hydrogen molecule are closely similar, making the interpretation of the inelastic neutron scattering data difficult. Finally, we show that the orientation of H_2 has a surprisingly large effect on the binding potential, reducing the classical binding energy by almost 30%. The implication of these results for the development of MOF materials for better hydrogen storage is discussed.

12. Size Effects on the Hydrogen Storage Properties of Nanoscaffolded $Li_3BN_2H_8$, Hui H. Wu, W. Zhou, K. Wang, T.J. Udovic, J.J. Rush, T. Yildirim, L.A. Bendersky, A.F. Gross, S.L. Van Atta, J.J. Vajo, F.E. Pinkerton, and M. S. Meyer, *Nanotechnology* 20, 204002 (2009).

The use of $Li_3BN_2H_8$ complex hydride as a practical hydrogen storage material is limited by its high desorption temperature and poor reversibility. While certain catalysts have been shown to decrease the dehydrogenation temperature, no significant improvement in reversibility has been reported thus far. In this study, we demonstrated that tuning the particle size to the nanometer scale by infiltration into nanoporous carbon scaffolds leads to dramatic improvements in the reversibility of $Li_3BN_2H_8$. Possible changes in the dehydrogenation path were also observed in the nanoscaffolded hydride.

Publications

**(DE-FG02-08ER46522,
Duration: 08/15/2008 – 04/30/2009)**

1. “High-Capacity Methane Storage in Metal-Organic Frameworks $M_2(dhtp)$: The Important Role of Open Metal Sites”, Hui Wu, Wei Zhou, and Taner Yildirim, *J. Am. Chem. Soc.* **131**, 4995 (03/10/2009).
2. “Hydrogen adsorption in HKUST-1: a combined inelastic neutron scattering and first-principles study”, C.M. Brown, Y. Liu, T. Yildirim, V.K. Peterson and C.J. Kepert, *Nanotechnology* **20**, 204025 (2009).
3. “Size effects on the hydrogen storage properties of nanoscaffolded $Li_3BN_2H_8$ ”, H. Wu, W. Zhou, K. Wang, T.J. Udovic, J.J. Rush, T. Yildirim, L.A. Bendersky, A.F. Gross, S.L. Van Atta, J.J. Vajo, F.E. Pinkerton and M.S. Meyer, *Nanotechnology* **20**, 204002 (2009).
4. “Methane Sorption in Nanoporous Metal-Organic Frameworks and First-Order Phase Transition of Confined Methane”, W. Hui, W. Zhou, and T. Yildirim, *J. Phys. Chem* **113**, 3029 (2009).
5. “Enhanced H_2 Adsorption in Isostructural Metal-Organic-Frameworks with Open Metal Sites: *Strong Dependence of the Binding Strength on Metal Ions*”,

W. Zhou, H. Wu, and T. Yildirim, *J. Am. Chem. Soc.* **130**, 15268 (2008).

6. “Alkali and Alkaline-Earth Metal Amidoboranes: Structure, Crystal Chemistry, and Hydrogen Storage Properties”, H. Wu, W. Zhou, and T. Yildirim, *J. Am. Chem. Soc.* **130**, 14834 (2008).

Publications

**DE-FG02-98ER45701,
Duration: 08/15/2008 – 07/01-2006)**

7. “Origin of the exceptional negative thermal expansion in metal-organic frameworks-5 $Zn_4O(1,4\text{-benzenedicarboxylate})(3)$ ”, W. Zhou, H. Wu, T. Yildirim, *Phys. Rev. B* **78**, 054114 (2008).
8. “Quasi-Free Methyl Rotation in Zeolitic Imidazolate Framework-8”, W. Zhou, H. Wu, T.J. Udovic, J.J. Rush, and T. Yildirim, *J. Phys. Chem. A* **112**, 12602 (2008).
9. “Structural variations and hydrogen storage properties of Ca_5Si_3 with Cr_5B_3 -type structure”, W. Hui, W. Zhou, T.J. Udovic, J.J. Rush, T. Yildirim, *Chem. Phys. Lett.* **460**, 432 (2008).
10. “Nature and tunability of enhanced hydrogen binding in metal-organic frameworks with exposed transition metal sites”, W. Zhou and T. Yildirim, *J. Phys. Chem. C* **112**, 8132 (2008).
11. “Metal-organic frameworks based on double-bond-coupled di-isophthalate linkers with high hydrogen and methane uptakes”, X.S. Wang, S.Q. Ma, K. Rauch, J.M. Simmons, D.Q. Yuan, X.P. Wang, T. Yildirim, W.C. Cole, J.J. Lopez, A. de Meijere, H.C. Zhou, *Chem. Mater.* **20**, 3145 (2008).
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People Working on The Project

1. **Jamie Ford (UPENN)**: Jamie has recently joined our hydrogen storage program, starting April 1, 2009. He is fully supported by this grant. Since UPENN received the DOE grant money in Dec. 2008, we were not able to hire someone earlier. Currently, we are about to hire a 2nd person to work on this project.
2. **Jason M. Simmons (NRC postdoc at NIST)**: Jason was employed at UPENN during the initial phase of this proposal (2007) but then he got NIST NRC postdoctoral research grant and therefore his salary is no longer supported by this DOE grant. He works part time on this project using Sievert equipment, chemicals, etc which are funded by this grant.
3. **Wei Zhou (University of Maryland and NIST)**: Wei got his PhD from UPENN on 2005. During 2005-2007, he worked as PostDoct with Dr. Yildirim and funded by DOE UPENN-Drexel-NIST EERE. Since 2007, Wei joined NIST permanently and works with Dr. Yildirim on this project as a valuable collaborator.
4. **Prof. Salim Ciraci (Bilkent, Turkey)**: We have a long term international collaboration for the computational portion of this work with Prof. Salim Ciraci at Bilkent University, Ankara, Turkey. Prof. Ciraci or someone from his group usually visit us during the summer for a month. This visit is supported by the DOE grant (i.e. per diem, hotel, rental car, etc).

IV.I.25 Integrated Nanoscale Metal Hydride – Catalyst Architectures for Hydrogen Storage

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1. Fabrication of Mg Nanoblades and Catalyst-Loaded Mg Nanostructures

We have designed and installed a unique GLAD system with two e-beam sources for the fabrication of nanostructured hydrogen storage materials (such as Mg, MgNi alloy, catalyst coated/doped Mg and its alloy, multilayered metal nanostructures). Due to the reactive nature of the metals/metal alloys for hydrogen storage, the system integrates the vacuum chamber with a glove box. This unique system shown in Figure 1 is the first of its kinds in the world.

Using the unique GLAD system, we have fabricated Mg thin film using normal deposition configuration,

FIGURE 1. The unique GLAD system designed for this project.

and Mg nanoblade by GLAD with an incident angle $\alpha \geq 70^\circ$. The as-deposited Mg film shows a typical columnar structure, and its surface consists of piles of nanoflakes, overlapping with one another. The as-deposited GLAD sample shows a well-aligned nanoblade array structure with a blade thickness of tens to hundreds of nm (similar to Figures 1a and b). The thickness of the Mg nanoblades along the incident vapor direction is markedly thinner than the width perpendicular to the incident vapor direction. In addition, by combining the GLAD technique with multilayer deposition and dynamic shadowing growth, one can deposit a thin layer of catalyst to coat the two sides of individual Mg nanoblades, and thus form catalyst decorated Mg nanoblade array structure. With two e-beam sources, a technique called glancing angle co-deposition (GLACD) can be used to fabricate catalyst-doped Mg nanostructures. The GLACD technique is a combination of co-deposition and GLAD. The co-deposition provides a way to evaporate two or more materials simultaneously to form composite or doped material, while the GLAD technique provides a way to form aligned nanorod arrays and to design the topological shape of the nanostructures. The composition of the resulting decorated/doped structures can be controlled by varying the relative ratio of deposition lengths/rates of two or more sources. We have demonstrated that when doped with a small amount of catalyst (like Ti or V), well-aligned nanorod array, not the nanoblades, formed. This may be due to the pinning of catalyst atoms for Mg adatoms diffusion.

Figures 2a-b and e-f show the top view and cross-sectional SEM images of the 4.6 at% V-decorated Mg nanoblades and V-doped Mg nanorods deposited at an incident angle of 70° , respectively. From the composition depth profiles of both nanostructures by EDX mapping their cross-sections (Figures 2c and g), it is clear that both Mg and V distribute almost uniformly throughout the entire nanostructure height. In order to visualize the difference of fine structure of V on/ in Mg matrix in both nanostructures, XRD, TEM and SAED were characterized. The results show that, for the V-decorated Mg nanoblades, the V exists in the form of randomly oriented crystals of ~ 5 nm diameter, in terms of the TEM (inset in Figure 2d), XRD (Figure 3a), and SAED (Figure 2d); while for the V-doped Mg nanorods, the V could exist in the Mg matrix in the form of atoms and/or very small clusters due to its undetectability by SAED (Figure 2h) and XRD (Figure 3b). Specifically, for the V-decorated Mg, the ED pattern (Figure 2d) is composed of the diffraction rings of V crystals and the diffraction spots of single crystal Mg; while for the

FIGURE 2. Top view and cross-section view SEM images of the as-deposited 4.6 at% V-decorated (a, b) and -doped Mg (e, f) nanostructures at 70°; (c, g) the composition depth profiles by EDX of the cross-sections b, f); the SAED patterns of V-decorated Mg nanoblade (d) and V-doped Mg nanorod (h); the inset in (d) is the TEM image, showing Mg matrix decorated with V particles of ~5 nm diameter.

V-doped Mg, only the diffraction spots of single crystal Mg appear in the ED pattern (Figure 2h). Their XRD results are shown in Figure 3. For both the as-deposited samples, the dominate XRD peaks are from hexagonal Mg, as shown in Figure 3a for the V-decorated Mg and Figure 3b for the V-doped Mg. However, there are three differences between them. First, the former has an extremely strong Mg (101) peak at $2\theta \approx 36.60^\circ$ compared to the latter. Second, by zooming in the Mg (101) peak shown in the top left inset, this Mg peak shifts toward a high diffraction angle $2\theta \approx 36.75^\circ$ in the V-doped Mg sample, implying that the V is indeed doped into the Mg matrix and thus produces a stress [3]. Third, by zooming in the patterns ranging from 39° to 45° shown in the top right inset, a broad and weak V signal around 42° is visible in the V-decorated Mg, corresponding to nanocrystalline V grains of ~5 nm in diameter by Scherrer's formula [7], but not in the V-doped Mg, indicating that the V element in the doped sample is doped in the Mg in the forms of atoms or very small clusters. These results show that using this unique two-source GLAD system, one can tailor and design sophisticated metal and alloy nanostructures with/without nanocatalysts for hydrogen storage applications.

The Design of Novel Ti Barrier to Prevent Mg_2Si Formation in the H-Cycling of Mg/Si

Our experiments have revealed that Mg_2Si alloy can form even at a temperature as low as $T = 200^\circ\text{C}$ when Mg is deposited directly on Si substrate. This reaction strongly affects the hydrogen storage reversibility and cycling performance, and prohibits a good understanding of intrinsic H-nanostructure interactions. To prevent Mg/Si alloying, we have designed and fabricated a unique Ti nanostructure diffusion barrier using the shadowing effect of the GLAD technique (Figure 4).

FIGURE 3. Typical XRD patterns of both nanostructures before and after H-cycling: (a) the as-deposited V-decorated Mg nanoblades; (b) the as-deposited V-doped Mg nanorods; (c) the hydrogenated and (d) the dehydrogenated V-doped Mg nanorods; (e) the hydrogenated V-decorated Mg nanoblades. The zoom-in patterns in the top left inset show the Mg peak shift to a higher angle due to the V-doping and its shift back after H-cycling. The zoom-in patterns in the top right inset show the difference and similarity in the as-deposited and H-cycled two nanostructures.

FIGURE 4. Design for a diffusion barrier layer composed of a Ti film and a Ti nanorod array on Si substrate, and then growing a layer of either Mg-based film (a) or nanoblade array (b) on top of the Ti nanorods.

We first deposited a 1 μm Ti film on the Si substrate, then a 500 nm Ti nanorods on the Ti film, followed by depositing Mg thin films or nanostructures directly on the Ti nanorod arrays, so that the Mg structures are lifted from the substrate. In fact, the V-decorated and doped Mg nanostructures in Figure 2 were grown on the unique Ti barriers, which can be seen in the cross-sectional SEM images (Figure 2) and detected by XRD. Our H-cycling experiments demonstrate that this Ti structure can endure over 15 hydrogenation-dehydrogenation cycles for the hydrogen storage kinetic and thermodynamic study of film-based Mg nanostructures with/without nanocatalyst. V-decorated

and -doped Mg nanostructures in Figure 2 were grown on the Si substrates with layers of 500 nm Ti nanorods at 70° and 1 μm Ti film at 10° in between the Mg samples and Si substrates. The Ti barrier can be seen in the cross-sectional SEM images (Figure 2) and detected by XRD (the inserted patterns of Figure 3).

MgH₂ Nanowire Formation during the Hydrogenation of Ti-Doped Mg Film

Once the Mg₂Si alloy formation is eliminated for hydrogenation of Mg thin film by the special barrier layer, new hydrogenation phenomenon has been observed during the hydrogenation of pure and Ti-doped Mg thin film. When 2 at% Ti-doped Mg film (with Ti barrier layers) has been hydrogenated at temperatures $T < 300^\circ\text{C}$ for approximately 150 h, tetragonal single crystal MgH₂ nanowires are formed on the surface of Ti-doped Mg film, as shown in Figure 5. Figure 5a exhibits sections of some long and thin nanowires. These nanowires are very smooth and uniform. And some nanowires are short and thick, as shown in Figure 5b. This particular nanowire grew out from the sample surface, and the protruded end became distorted. The nanowires have diameters in the range of 200–700 nm, and most of them are below 400 nm. Also, for the wires thinner than 400 nm, the nanowires can grow very long, with lengths up to 500 μm or longer, while for those thicker than 400 nm, the nanowires are very short, only tens of microns or even shorter. The crystal structure and composition of the nanowires are confirmed to be tetragonal single crystal MgH₂ by XRD, Raman spectroscopy, EDX and TEM. Figure 5c shows a typical Raman spectrum obtained from the hanged nanowires in the inserted image. There are three Raman peaks centered at 312, 954, and 1,279 cm^{-1} , respectively. The 312 cm^{-1} and 954 cm^{-1} peaks are strong and sharp, while the 1,279 cm^{-1} peak is relatively weak and broad with a shoulder at its low wave-number side. The three peaks correspond to the characteristic vibration modes, B_{1g} , E_g , and A_{1g} , of tetragonal MgH₂. Our results show that the hydrogenation time and temperature are the two main factors for the nanowire formation.

The Hydrogenation and Dehydrogenation of V-Decorated and Doped Mg Nanostructures

The V-decorated and -doped Mg nanostructures were respectively installed in a PCT Sievert's-type apparatus (Hy-Energy, PCTPro-2000) for H-absorption (under 10-bar H-pressure) and desorption (under vacuum) cycling measurements. Their H-sorption kinetics were measured at various temperatures below 300°C, and the sorption rate constants k at different temperature were calculated and are plotted with respect to inverse temperature $1/T$ in Figures 6e and f, for the hydrogen absorption and desorption processes. From

FIGURE 5. Typical top view SEM images of the hydrogenated 2 at% Ti doped Mg film sample showing (a) nanowires and (b) one whole nanowire formed on the sample surface. (c) Raman spectra obtained from individual nanowires shown by an inserted image.

FIGURE 6. Top view and cross-section view SEM images of V-decorated (a, b) and -doped (e, f) Mg nanostructures at 70° after hydrogen cycling; Arrhenius plots of (e) H-absorption and (f) H-desorption rate constant k versus reciprocal temperature $1/T$ for both the 4.6 at% V-decorated and -doped Mg nanostructures. The calculated H-desorption k values, based on our proposed phenomenological model, are displayed in (f) by the solid circles and solid squares.

the Arrhenius plots in Figures 6e and f, we obtain that the activation energy of the 4.6 at% V-decorated Mg

sample is $E_a^a = 51.7 \pm 0.9$ kJ/mol H_2 for absorption process and $E_a^d = 63.2 \pm 0.4$ kJ/mol H_2 for desorption process, and the activation energy of the 4.6 at% V-doped Mg sample is $E_a^a = 35.8 \pm 0.9$ kJ/mol H_2 and $E_a^d = 38.9 \pm 0.3$ kJ/mol H_2 . On one hand, these activation energies are much lower than the reported desorption energy of 141 kJ/mol H_2 for MgH_2 film and 156 kJ/mol H_2 for MgH_2 powder, indicating the catalytic effect of the incorporated V catalyst; on the other hand, the hydrogen sorption is faster for the V-doped Mg than the V-decorated Mg sample, and also the former has lower absorption and desorption activation energies than the latter, even though the V-decorated Mg (with a void ratio of ~668%) is more porous than the V-doped Mg structures (with a void ratio of only ~34%). After multiple cycles of hydrogen absorption/desorption, a significant morphology change occurs to both samples and they both present a very similar appearance: the original blade or rod structure is totally distorted to form aggregates of sphere-like particles, as shown by the SEM images in Figures 6a-b for the hydrogenated V-decorated Mg and Figures 6c-d for the hydrogenated V-doped Mg.

Figure 7 shows the obtained Arrhenius plots for the V-doped Mg nanostructures deposited at incident angles of 10° , 50° , and 70° . For the three nanostructures, the void ratio is estimated to ~4% of 10° , 14% of 50° , and 34% of 70° samples, respectively. From Figure 7, one can see that the hydrogen sorption becomes faster and faster with increasing the deposition angle or the porosity; the H-absorption activation energy decreases from $E_a^a = 51.4 \pm 1.5$ kJ/mol H_2 of the 10° sample, $E_a^a = 47.0 \pm 1.4$ kJ/mol H_2 of the 50° sample, to $E_a^a = 35.8 \pm 0.9$ kJ/mol H_2 of the 70° sample (Figure 7a); the hydrogen desorption activation energy decreases from $E_a^d = 69.4 \pm 0.6$ kJ/mol H_2 of the 10° sample, $E_a^d = 64.8 \pm 0.4$ kJ/mol H_2 of the 50° sample, to $E_a^d = 38.9 \pm 0.3$ kJ/mol H_2 of the 70° sample (Figure 7b). The improved hydrogen sorption performance could be caused by the smaller particles/grains with increasing the deposition angle.

FIGURE 7. Arrhenius plots of (a) H-absorption and (b) H-desorption rate constant k versus reciprocal temperature $1/T$ for the 4.6 at% V-doped Mg nanostructures at 10° , 50° , and 70° .

5. FRES and RBS Results

FRES (forward recoiled spectrometry) measurements on metal hydride films have been carried out using the ion beam facility at UPenn (with Prof. Howard Wang). In FRES, a collimated 3.0 MeV He^{2+} beam incident on samples at 75° from the surface normal, recoiled H atoms were detected at the specular reflection direction, while the forward scattered He ions were stopped using a 12 μ m thick aluminum foil. Figures 8a and b show FRES spectra of 4 μ m pure Mg films and nanoblades after hydrogenation at various temperatures, respectively. The H uptake in Mg films is rather minimal at 300° C and below, whereas significant absorption of H in nanoblades occurs at a temperature as low as 200° C, suggesting lower activation barrier due to the large surface area. Figure 8(c) reveals slight H enrichment near film surfaces at low-T, possibly due to the water adsorption. The integrated total H uptake for two series is shown in Figure 8(d). It is apparent that activation of H absorption occurs at a lower T in Mg nanoblades, although the H saturation in nanoblades is lower.

6. Neutron Scattering Results

PGAA (prompt gamma-ray activation analysis) measurements have been carried out on V-doped and decorated Mg nanoblades in NIST by Prof. Howard Wang. A typical PGAA spectrum is shown in Figure 9, where characteristic activation peaks are used to identify the absolute amount of H, Mg and V in those samples. Careful analysis shows chemical stoichiometry of Mg:H:V = $(1.00 \pm 6.13\%) : (1.72 \pm 1.04\%) : (0.0428 \pm 1.48\%)$ in the V-decorated sample and Mg:H:V = $(1.00 \pm 5.15\%) : (2.00 \pm 1.01\%) : (0.0515 \pm 1.29\%)$ in the V-doped sample, respectively. Note the high accuracy

FIGURE 8. FRES measurements of hydrogen profiles of (a) Mg films and (b) Mg nanoblades after hydriding at various T. (c) The surfaces enrichment in films of low-T treatment. (d) Total H uptake for both films and nanoblades.

FIGURE 9. The PGAA spectrum of V-doped MgH_x nanoblades. Insets show the characteristic γ -ray emissions for quantifying each element.

of absolute H quantification using PGAA. Within the experimental error, the theoretical limit of H absorption was reached in V-doped Mg nanoblades at a rather mild hydrogenation condition. Small angle neutron scattering (SANS) has also been used to measure the samples. The dominant characteristics are the Q^{-3} power law scaling in both samples, indicating 3D “cardhouse” packing, consistent with nanoblade structure shown in Figure 2.

7. In Situ Temperature-Dependent Raman Spectroscopy Measurements

Hydrogenated Mg nanostructures were investigated using temperature-dependent Raman spectroscopy. The Mg film substrates were fabricated by UGA using OAD at an incident vapor flux of 9.9°. The most prominent peak at 951 cm^{-1} becomes increasingly broadened as the temperature reaches 150°C and above, but is still present at 180°C. The center peak position did not shift in a noticeable manner but the peak clearly became broader as the temperature was increased. When the temperature is returned to room temperature, the peak recovers, indicating no thermal degradation of the sample. The lack of peak shifting indicates that even at these high temperatures, the lattice is not being distorted by expansion or anharmonic effects. The broadening of the band is understandable since higher temperature shortens the lifetimes of the excited vibrational or phonon states, which leads to spectral broadening. In conclusion, temperature-dependent Raman characterization helped to provide a more fundamental look into the effect of temperature on the hydrogen-Mg interaction for this sample.

Using the temperature and pressure controlled in situ Raman chamber, layered magnesium films (Mg rods/Ti barrier layer/Si wafer substrate) fabricated by UGA were investigated to see if the hydrogenation of the sample could be monitored with Raman spectroscopy. Unfortunately, higher temperatures

are needed to induce an observable amount of MgH₂ formation through Raman spectroscopy and our current chamber has limitations of both temperature (250°C) and pressure (100 psi) which inhibit our ability to monitor the hydrogenation and the dehydrogenation of the hydrogenated films. Extended periods of times were used at the chamber’s maximum temperature and pressure but no hydrogen sorption was observed. Future adjustments will be made to the chamber to ensure a wider range of temperatures which could aid the fundamental understanding of such materials and thus help to eventually lower those dehydrogenation temperatures.

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Personnel Associated with the Research

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Dr. Matthew D. McCluskey (co-PI)		

V. FUEL CELLS

V.0 Fuel Cells Sub-Program Overview

Introduction

The Fuel Cells Sub-Program supports research, development, and demonstration of fuel cell systems, including fuel cell stack components, fuel processors for stationary applications, and balance-of-plant (BOP) components. The portfolio of projects covers a broad range of technologies including polymer electrolyte membrane fuel cells (PEMFCs), direct methanol fuel cells and solid oxide fuel cells (SOFCs). The sub-program has shifted its main focus from long-term transportation to near-term applications of fuel cells, including distributed power (primary and backup), portable power, auxiliary power units (APUs), materials handling equipment, and specialty vehicles. Fuel cell technology already provides sufficient performance and durability to be competitive with alternative technologies in some of these applications, while in others modest improvements are required. Commercialization of fuel cells and deployment in these early-market applications is expected to lead to further improvement in performance, durability, and cost, while inducing growth in the domestic fuel cell manufacturing and supplier base. In the long term, continuing technological progress will allow fuel cells to expand into applications and markets that have more stringent technical and cost requirements. The growth of current markets and expansion into broader markets, including the light-duty vehicle market, will allow fuel cell technologies to have significant economic, energy security, and environmental benefits on a national scale.

As part of the American Recovery and Reinvestment Act, 13 new projects were initiated in Fiscal Year 2009 to accelerate the commercialization and deployment of fuel cells. The new funding will support immediate deployment of fuel cell systems in emergency backup power, portable, material handling, and combined heat and power (CHP) applications. The DOE funding for these projects is approximately \$42M. An additional 28 new projects were initiated following a 2008 solicitation/lab call. These projects include research and development (R&D) for catalysts with reduced Pt-group metal (PGM) content, as well as PGM-free catalysts. New projects also include fuel cell degradation and durability studies, fuel cell transport studies, portable power R&D, and development of innovative fuel cell concepts. The DOE funding for these projects is approximately \$113M.

Goal

Develop and demonstrate fuel cell power system technologies for stationary, portable, and transportation applications.

Objectives

- By 2011, develop a distributed generation PEMFC system operating on natural gas or liquefied petroleum gas that achieves 40% electrical efficiency and 40,000 hours durability at \$750/kW.¹
- By 2010, develop a fuel cell system for consumer electronics (<50 W) with an energy density of 1,000 Wh/L.
- By 2010, develop a fuel cell system for APUs with a specific power of 100 W/kg and a power density of 100 W/L.
- By 2010, develop a 60% peak-efficient, durable, direct hydrogen fuel cell power system for transportation at a cost of \$45/kW; by 2015, a cost of \$30/kW.

FY 2009 Technology Status

The focus of the sub-program is on materials, components, and enabling technologies that will contribute to the development of low-cost, reliable fuel cell systems. Cost and durability are the major challenges for fuel cell systems. Air, thermal, and water management for fuel cells are also key issues. Power density and specific power are approaching targets, but further increases are needed to meet

¹ Milestone delayed from 2010 to 2011 due to appropriations shortfall and Congressionally directed activities.

packaging requirements of commercial systems. Efforts continue to evaluate, understand, and mitigate degradation mechanisms by the national laboratories, universities, and fuel cell developers. These efforts are being enhanced by the use of advanced imaging techniques for in situ and post-mortem analysis of fuel cell stacks and membrane electrode assemblies.

The tasks in the Multi-Year Research, Development and Demonstration Plan, to be updated in 2009, are organized around components (membranes, electrodes, membrane electrode assemblies (MEAs), gas diffusion layers, bipolar plates, seals, and BOP components), supporting analysis, and benchmarking and characterization activities. Task areas are also included for early market fuel cell applications including stationary, portable power, and APUs, and for development of innovative concepts for fuel cell systems.

Targets, which vary by application, have been established for metrics such as fuel cell cost, efficiency, durability, power density, specific power, transient response time, and start-up time. Key performance indicators include cost for transportation fuel cells R&D and electrical efficiency for stationary fuel cells R&D. As shown in Figure 1, the cost of a hydrogen-fueled 80-kW_e fuel cell power system projected for high volume production (500,000 units/year) has been estimated to be \$73/kW (assuming 2008 technology), a 23% reduction from the 2007 cost of \$94/kW. The assessment was validated by an independent review panel in FY 2009.² Cost reduction was a result of stack component costs being reduced through ongoing R&D efforts. As stack costs are reduced, BOP components are responsible for a larger percentage of costs.

For stationary systems, on-going projects show good progress toward higher electrical efficiency, lower cost and improved durability. At the same time, targets for both stationary and portable applications are being reassessed in accordance with realistic commercialization requirements and with feedback from stakeholders and experts in the field. In this respect, a Request for Information was issued seeking input from stakeholders and the research community on proposed performance, durability, and cost targets for fuel cells for residential CHP applications and APUs. The targets are driven by consumer expectations for CHP and APU applications, rather than by the operating parameters or constraints of specific technologies.

²The report of the independent review panel is available at <http://www.nrel.gov/docs/fy09osti/45457.pdf>.

FIGURE 1. Current Modeled Cost of an 80-kW System Based on Projection to High-Volume Manufacturing (500,000 units/year)

FY 2009 Accomplishments

Continued progress toward meeting 2010 and 2015 technical and cost targets occurred during FY 2009. Notable technological advances in several component areas have led to significant improvements in performance and durability, with decreased cost.

Innovative Catalyst and MEA R&D Enables Lower Fuel Cell Cost

Decreases in fuel cell system cost are, to a large extent, limited by the high catalyst cost associated with the use of Pt and other PGMs. Reducing the loading of Pt and other PGMs, without compromising performance, is therefore a key path to decreasing system cost. Notable progress in developing catalysts with high activity at low loading was made during 2009 at Brookhaven National Laboratory (BNL), where novel core-shell electrocatalyst structures are being investigated for application in fuel cell cathodes. Innovative new PGM-based nanostructured catalysts developed at BNL in FY 2009, consisting of a Pt shell, a core containing PGMs other than Pt, and a Pd interlayer in between the core and the shell, have high activity for the oxygen reduction reaction (ORR). The ORR performance of these new catalytic materials at 0.9 V is as high as 1.2 A/mg_{Pt} and 0.34 A/mg_{PGM}, comparing favorably with the baseline Pt/C catalyst activity of 0.13 A/mg_{Pt}. These new catalysts also show better durability than previously reported core-shell materials and state-of-the-art Pt/C catalysts. For example, a Pt_{ML}/Pd_{ML}/Pd₃Ir/C catalyst has been shown to lose approximately 20 mV in ORR performance after 30,000 potential cycles, compared to approximately 40 mV lost by a standard Pt/C catalyst under the same conditions. Even lower performance losses have been demonstrated with other core-shell catalysts, including a Pt_{ML}/Pd₃Fe/C catalyst, with an ORR performance loss of less than 5 mV after 28,000 potential cycles. While most core-shell catalysts to date have been synthesized in small, laboratory-scale batches, *Cabot Fuel Cells* demonstrated industrial scale-up of Pt-Pd/C core-shell catalysts to gram-scale quantities in 2009, maintaining the catalyst's superior performance relative to Pt. These and other advancements in PGM-based catalysts represent significant progress in 2009 toward improvement of fuel cell performance and reduction in fuel cell cost through minimization of PGM loading.

Efforts to further reduce or even eliminate PGMs from cathode catalysts also showed progress in 2009. Los Alamos National Laboratory (LANL) developed two independent paths toward high-performance PGM-free fuel cell cathodes, based on Fe₃Co/polyaniline/C and Fe/cyanamide/C catalysts with volumetric activities of 27 and 54 A/cm³ at 0.80 V, respectively. These activities represent a five-fold and an eleven-fold improvement over the most active non-noble catalyst investigated as of the previous year. With plans for further optimization of the catalyst compositions, as well as major modification of the as yet unoptimized electrode structures, the program is on track to meet the 2010 non-PGM catalyst activity target of 130 A/cm³.

3M has played a significant role in the major reduction in fuel cell system cost achieved over the past few years. Ongoing R&D at 3M in 2009 led to further decreases in PGM loading, and reduction in cost, with improvement in performance and durability. In 2009, 3M demonstrated a new baseline MEA with PGM loading of 0.15 mg/cm², a 40% decrease in loading since 2008. On a power-specific basis, the new baseline loading is 0.18 g/kW, a 33% decrease in loading since 2008. In single-cell testing, the new baseline MEA loading is already below the 2015 target levels of 0.2 mg/cm² and 0.2 g/kW. The continued success of 3M in achieving better performance with lower PGM loading has allowed precious metal content to be decreased to within an order of magnitude of that used in automotive internal combustion engine systems. The successful use of such low PGM loadings indicates that large-scale implementation of durable, high-performance automotive fuel cell systems will not require an increase in PGM production to levels far beyond the scale of current mining and extraction operations. Progress by 3M and others in reducing PGM loading over the last five years is illustrated in Figure 2. The recent success of 3M in achieving very good performance at low catalyst loading is augmented by demonstration of the excellent durability of 3M MEAs. In addition to achieving 7,300 hours of operation under voltage cycling, as reported in 2008 and duplicated in 2009, the 3M MEA exceeded DOE's set lifetime targets for minimal surface area and performance loss under open circuit voltage hold tests by more than 300%.

FIGURE 2. State-of-the-art total PGM loading in a fuel cell stack as determined by USCAR Fuel Cell Tech Team. DOE targets are also shown for comparison. 2009 data is a projection based on single-cell testing.

Innovative Membrane Materials Achieve High Conductivity under Hot, Dry Conditions

Current fuel cells containing state-of-the-art perfluorosulfonic acid (PFSA)-based membranes require humidification of inlet streams. The necessary humidification system represents a major component of fuel cell system cost. Work is underway to develop high-temperature membranes capable of operating at low relative humidity (RH), which would decrease or eliminate the cost, bulk, and system complexity associated with humidification. Major progress in development of such membranes occurred during FY 2009. *Giner Electrochemical Systems* demonstrated a dimensionally-stabilized low equivalent weight PFSA membrane with conductivity at least 2.5 times that of Nafion[®] under hot, relatively dry conditions, exceeding the DOE 2009 conductivity milestone of 0.1 S/cm at 120°C and 50% RH. Low-RH conductivity greatly exceeding that of Nafion[®] was also demonstrated at *Case Western Reserve University*, where a rigid-rod PEM was developed with conductivity *100 times that of Nafion[®]* at 15% RH. Nanofiber composite network PEMs developed at *Vanderbilt* demonstrate another path toward meeting set DOE membrane performance targets, with an inorganic-doped low equivalent weight PFSA nanofiber network providing conductivity meeting the DOE 2009 conductivity milestone, while an inert polymer matrix provides excellent mechanical properties.

Impurities Projects Assist in the Development of Fuel Purity Standards

As fuel cells approach a level of development that can support commercialization, real-world issues such as the development of fuel purity standards have received increased attention. Research at LANL on the effect of impurities on fuel cell performance and durability contributes to this effort. In FY 2009, LANL examined the effects on fuel cell performance and durability of potential hydrogen contaminants including H₂S, hydrocarbons, and NH₃. At levels likely to be present in H₂ fuel, common C₁-C₃ hydrocarbons (ppm levels) were found to have minimal impact on fuel cell performance. In contrast, ppm levels of NH₃ in the fuel inlet stream were found to result in significant performance degradation through cationic poisoning of the membrane and/or electrode ionomer. Studies of the NH₄⁺ removal mechanism revealed negligible electrochemical oxidation, with removal of dissolved NH₄⁺ in the water effluent from the fuel cell representing the largest contribution to the slow performance recovery following exposure to NH₃. Similarly, sub-ppm levels of H₂S in H₂ fuel also caused significant performance loss, with degradation occurring due to catalyst poisoning in both the anode and the cathode. The ability of a contaminant in the anode inlet to cause degradation of the cathode demonstrates the important role of contaminant crossover in performance degradation. In addition to examining potential fuel impurities, potential air impurities, including SO₂ and NO₂, were examined, revealing significant performance degradation due to catalyst poisoning. Potential contaminants arising from corrosion of fuel cell stack components, including metal ions, were found to cause major performance degradation due to membrane/ionomer poisoning, validating cation impurity models.

developed as a part of the project. These efforts in impurities testing will assist in identifying permissible levels of contaminants in H₂ fuel, as well as identifying operating conditions and component designs to optimize fuel cell performance and mitigate the effects of impurities from H₂ fuel and other sources.

Pt Recycling: Increased Yield at Lower Process Cost

Since the Pt cost is a large fraction of total system cost, Pt recovery during fuel cell disposal is a critical aspect of cost reduction. With the value of Pt in used MEAs on the order of \$300 per kg of MEA material, based on an estimated Pt cost of \$1,000 per troy ounce, effective Pt recovery is imperative. R&D at BASF on efficient, low-cost Pt recycling has yielded a method of Pt recovery involving either granulating or cryo-milling, followed by a single-step oxidative leaching procedure. The simplified leaching process can be performed in a single vessel. Both preparation techniques enable *cost effective recovery of 98% of Pt* from used MEAs without hydrogen fluoride release. Operated commercially, the processes require little manual labor and generate minimal waste (solid residue of the leached MEAs).

Successful International Collaboration Demonstrates Development of Commercial CHP Fuel Cell System

Plug Power's NextGenCell project, which involved a significant collaboration and cost-sharing between the U.S. and the European Union, was completed in 2009. The project resulted in the development of a high temperature, stationary, reformat-based PEM CHP fuel cell system based on commercial requirements. The project enabled MEA, stack, reforming and power electronics technologies to be explored, down-selected and developed, with progress made toward achieving DOE technical targets. By the end of the project, design verification testing against commercial requirements was completed.

Demonstrated Fuel Cell Technology for APU Applications

In 2009 a Delphi APU employing an SOFC successfully powered the electrical system and air conditioning of a Peterbilt Model 386 truck under conditions simulating a 10-hour night. The device provides an alternative to running a truck's main diesel engine to power auxiliary electrical loads during rest periods, thereby lowering emissions of CO₂ and criteria pollutants, reducing noise, and saving fuel.

Budget

The President's 2010 budget request (subject to Congressional appropriation) calls for approximately \$63M for the Fuel Cells sub-program, and emphasizes R&D on materials, stack components, BOP subsystems, and integrated fuel cell systems for stationary, portable, and transportation applications. Examples of applications include distributed CHP fuel cells, APUs to reduce fuel consumption and emissions in heavy-duty vehicles, small fuel cells for portable power, and fuel cells as backup power for critical infrastructure. A technology-neutral approach is pursued, and multiple primary fuel sources are considered, including bio-derived renewable fuels such as methanol, fuels derived from other renewable resources, and fossil fuels such as diesel and natural gas. Figure 3

FIGURE 3. 2009 Congressional Appropriation and 2010 Budget Request

shows the 2010 budget request in comparison to the sub-program topic breakdown of the 2009 Congressional appropriation.

2010 Plans

In FY 2010, R&D activities will be focused on developing fuel cells suitable for use in several key applications, as well as improving component properties for key fuel cell technologies. Catalyst R&D activities will include PGM-based and non-PGM catalyst systems. The focus of PGM-based catalyst R&D will be on approaches that increase activity and utilization of current PGM and PGM alloy catalysts. Non-PGM catalyst investigations will focus on providing a better understanding of catalytically active sites and determining the oxygen reduction reaction mechanisms on these sites. Activities will also include investigation of durable catalysts to enhance stability under start-stop conditions. In situ studies will examine the effects of catalyst-support interactions, catalyst particle size, and catalyst structure. Innovative fuel cell component structures will also be investigated. Non-carbon support projects will develop materials with superior corrosion resistance and with electrical and structural properties that exceed the properties of carbon.

Work will continue on development of high-temperature membranes that reduce the need for humidification, allow better catalyst performance, reduce the negative effects of impurities, and decrease the size of the cooling system. Further R&D activities will include development of high-performance MEAs that incorporate the advanced membrane materials developed in FY 2009. Work will also continue on development of bipolar plates and seals that are inexpensive and corrosion resistant. In addition, R&D on gas diffusion layers will continue, improving water management characteristics and enhancing fuel cell performance.

Research on fuel cell system degradation will include development of integrated degradation models at the component, interface, and cell levels. The performance of MEAs in single cells and short stacks will be evaluated, and progress will be compared to DOE targets. Investigation and quantification of the effects of impurities on fuel cell performance will continue, including parametric studies of the effect of poisons on cell performance and durability, identification of poisoning mechanisms and recommendations for mitigation, and modeling of impurity effects on cell performance and durability. Results will provide further input on development of fuel cell standards.

Water management R&D will focus on the development of novel humidification materials that are inexpensive, durable, and able to support high performance operation in all operating environments, while meeting size and weight restrictions. Projects will examine concepts for novel water management devices and fuel cell system configurations that facilitate water management. Fuel cell system performance modeling will assist in optimization of water management devices and system configurations. Third-party evaluation of fuel cell stacks and systems will increase as these technologies mature.

Portable power R&D will focus on reducing anode and cathode catalyst loadings, while improving power density. R&D will also be directed toward development of membranes with increased proton conductivity, reduced methanol crossover, and improved water management. New R&D work on innovative anion-conducting low-temperature fuel cells will be initiated, with potential uses in portable power and other fuel cell applications. The focus of this work in FY 2010 will be on development of novel membrane materials with high anionic conductivity and high chemical stability.

Auxiliary power R&D will focus on developing fuel cell systems for heavy-duty trucks. Cell conductivity, catalyst performance, and chemical degradation issues will also be addressed. As targets are re-evaluated with feedback from stakeholders and the research community, a more pragmatic progress assessment will be made. In FY 2010, SOFC hardware will be tested for potential application as an APU on heavy-duty trucks. Results from these tests will help to assess the impact of the critical issues on SOFC performance and to direct future R&D efforts.

The sub-program's effort in facilitating fuel cell technology development for CHP applications will continue and be expanded. This will involve a 'technology-neutral' stance where PEMFC, SOFC, and other fuel cell technologies are included. In similar fashion to DOE's cost analysis approach to fuel cells for light-duty vehicle applications, current cost will be projected and independently validated for

CHP applications, targets for cost, performance, and durability will continue to be updated, and R&D needs will continue to be identified.

Sub-program activities will include promoting early adoption of fuel cell systems to validate performance, durability, and reliability through field testing. These efforts will lead to cost reduction and an increase in fuel cell stack durability, enabling fuel cells to transition from a niche market to a robust portfolio of applications, allowing the economic and environmental benefits that are shown in niche applications to expand into larger markets.

FY 2010 will see the continuation of existing projects and of those awarded in FY 2009, as well as a new initiative focusing on addressing urgent issues regarding near-term applied fuel cell technology. As technical targets are reassessed, R&D needs will be defined. Decreased cost with enhanced performance and durability would allow increased commercialization in early markets, enabling progress in fuel cell technology for more challenging, long-term applications. As stack component cost reduction continues, BOP component R&D will increase to facilitate an overall decrease in system cost. As the sub-program's direction extends further beyond direct H₂ PEMFCs, R&D needs for the advancement of alkaline and other fuel cell technology will also be examined.

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V.A.1 Fuel Cell Systems Analysis

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Project End Date: Project continuation and
direction determined annually by DOE

Objectives

- Develop a validated model for automotive fuel cell systems, and use it to assess the status of the technology.
- Conduct studies to improve performance and packaging, to reduce cost, and to identify key research and development issues.
- Compare and assess alternative configurations and systems for transportation and stationary applications.
- Support DOE/FreedomCAR automotive fuel cell development efforts.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells, and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (B) Cost
- (C) Performance
- (E) System Thermal and Water Management
- (F) Air Management
- (G) Startup and Shutdown Time and Energy/Transient Operation

Technical Targets

This project is conducting system level analyses to address the following DOE 2010 and 2015 technical targets for automotive fuel cell power systems operating on direct hydrogen:

- Energy efficiency: 50%-60% (55%-65% for stack) at 100%-25% of rated power
- Power density: 650 W/L for system, 2,000 W/L for stack
- Specific power: 650 W/kg for system, 2,000 W/kg for stack
- Transient response: 1 s from 10% to 90% of rated power
- Start-up time: 30 s from -20°C and 5 s from +20°C ambient temperature
- Precious metal content: 0.3 g/kW (2010), 0.2 g/kW (2015)

Accomplishments

- Worked with 3M to analyze the performance of stacks with nanostructured thin film catalysts (NSTFCs) with reduced Pt loading and at elevated temperatures.
- Built and validated the performance maps for the different components of the Honeywell's integrated compressor-expander-motor module (CEMM) and analyzed the performance of the CEMM.
- Analyzed the performance of advanced automotive radiators with high-density louver and plain microchannel fins. Identified a compact radiator design with the lowest parasitic air pumping power.
- Assisted Honeywell in determining the performance of full-scale enthalpy wheel and membrane humidifiers (MHs).
- Determined the time and energy for startup and shutdown of polymer electrolyte fuel cell stacks at different stack and ambient temperatures.
- Conducting drive cycle simulations to determine the fuel economy of hybrid fuel cell vehicles.

Introduction

While different developers are addressing improvements in individual components and subsystems in automotive fuel cell propulsion systems (i.e., cells, stacks, balance-of-plant components), we are using modeling and analysis to address issues of thermal and water management, design-point and part-load operation, and component-, system-, and vehicle-level efficiencies and fuel economies. Such analyses are essential for effective system integration.

Approach

Two sets of models are being developed. The GCtool software is a stand-alone code with capabilities for design, off-design, steady state, transient, and constrained optimization analyses of fuel cell systems (FCSs). A companion code, GCtool-ENG, has an alternative set of models with a built-in procedure for translation to the MATLAB/SIMULINK platform commonly used in vehicle simulation codes such as PSAT.

Results

In Fiscal Year 2009, we changed our reference FCS configuration (see Figure 1) to provide for cooling of the motor and airfoil bearings (AFBs) in the CEMM, and replaced the enthalpy wheel humidifier with a membrane humidifier for the cathode inlet air [1]. The revised configuration also includes an air precooler upstream of the MH for improved MH durability and performance.

Air Management

We analyzed data received from Honeywell and constructed performance maps for the mixed axial flow compressor, variable area nozzle turbine (VNT), 3-phase brushless direct current motor, and liquid-cooled motor controller [2]. We also developed correlations for the motor and AFB cooling loads and pressure drops for the motor/AFB cooling air and the CEMM air filter. The maps were used to model the performance of a matched compressor, expander, and motor on a common shaft for the 80-kW reference FCS: 2.5 bar at rated power, 90°C stack temperature, 91 g/s dry air flow rate, and 3 psi pressure drop between the compressor exit and turbine inlet. We determined the VNT nozzle area and shaft rpm to control the stack inlet relative humidity (RH) with a membrane humidifier. Figure 2 presents the modeled operating map of the CEMM and the component efficiencies. The calculated peak efficiencies are 70.3% for the compressor, 73.2% for the expander, 86% for the motor and 87.3% for the motor controller, which may be compared with the efficiency targets of

FIGURE 1. Reference Pressurized FCS with Motor Cooling and Membrane Humidifier

80% each for the compressor and the expander, and 92% each for the motor and the motor controller. We calculate that for the FCS at rated power, the CEMM will consume about ~9 kW at 300 K ambient temperature, significantly higher than the target power consumption of 4.4 kW.

Fuel Cell Stack Performance

We received 3M single-cell data for the electrochemical surface area, specific activity, short and crossover currents and high frequency resistance over a wide range of temperatures (80–120°C) and RHs (20–100%) [3]. The data, obtained with 0.1(a)/0.15(c) mg/cm² Pt loading and 35- μ m-thick membrane (850 equivalent weight), provided a basis for formulating a kinetic model for the oxygen reduction reaction (ORR) on the nanostructured thin film ternary PtCoMn catalyst that is valid at elevated temperatures and under dry conditions. The ORR kinetics model was used in a trade-off study to determine the stack Pt content (g/kW) as a function of the operating pressure, temperature and inlet RH for specified system efficiency (50%), oxygen utilization (50%) and per-pass hydrogen utilization (70%). The results from the study (Figure 3) showed that for a given stack inlet pressure, the Pt content is at a minimum corresponding to an optimum level of RH that is a function of the stack operating temperature (e.g., 40% RH at 90°C and 2.5 bar). The higher the stack temperature, the higher is the optimum RH. Moreover, for a given stack inlet pressure there is an optimum combination of stack temperature and RH that leads to a minimum Pt content (100°C and 50% RH at 2.5 bar). In practice, however, the maximum stack operating temperature will likely be limited by the membrane and catalyst durability concerns.

The study was expanded by varying the stack pressure over the range 1.25 to 2.5 bar. The optimum combinations of stack temperature and inlet RH were determined as a function of the stack inlet pressure. We found that the optimum stack temperature increases, and the inlet RH decreases, as the stack inlet pressure is raised. For the conditions of this study, the optimum combination of temperature and inlet RH is 94°C and 52% at 2 bar and 82°C and 58% at 1.3 bar. We calculated that the air management system consumes

FIGURE 2. Performance of Integrated CEMM with VNT and Motor Cooling

FIGURE 3. Effect of NSTFC Stack Operating Pressure on Temperature and RH (a), Pt Content (b) and Power Density (c)

9 kW to deliver air at 2.5 bar stack inlet pressure but only 5.2 kW if the stack inlet pressure is reduced to 1.3 bar. As a result, the stack operating at 2.5 bar has to generate ~3.8 kW additional power to compensate for the larger parasitic losses (constant 80 kW net system power) and to operate at ~30 mV higher cell voltage to maintain constant 50% system efficiency. In spite of these drawbacks, the stack power density is 35% higher at 2.5 bar than at 1.3 bar operating pressure and the overall Pt content is ~30% lower. This study leads to the conclusion that from the standpoint of reducing the overall Pt content (i.e., reducing the system cost), it is preferable to operate the NSTFC stack at a moderately high pressure (2.5 bar) than at low or near ambient pressures.

Thermal Management

We received and analyzed the thermal and fluid mechanics data from Honeywell for 9"x9" subscale radiators with 18 and 24 fpi (fins per inch) louver fins (LV) and 40 and 50 fpi plain microchannel (MC) fins [4]. We derived the friction factor (f factor) and heat transfer (j factor) coefficients from the data, formulated correlations for the f and j factors, and incorporated these correlations in our automotive radiator model. We compared the relative performance of the four fin geometries tested and concluded that the LV-24 fins are preferable to the LV-18 fins, and that the MC-40 fins are superior to the MC-50 fins. Our preliminary assessment of the 24-fpi louver and 40-fpi microchannel fins is that for a given frontal area ($A_{\text{ref}} = 0.25 \text{ m}^2$), heat load (50 kW at 55 mph) and reference grill and under-hood fluid mechanics parameters, the LV-24 fins require lower fan power but the radiator with MC-40 fins can be more compact.

We conducted a study to assess the heat rejection in fuel cell vehicles as a function of the stack and ambient temperatures. We considered that the air-conditioning condenser (8.5 kW heat load) and the low-temperature radiator (9 kW heat load) are stacked in front of the high-temperature radiator that rejects waste heat generated in the fuel cell stack. Figure 4 presents some of the results from the study for LV-24 fins. It shows that for a given frontal area, there is an optimum radiator depth that leads to minimum fan pumping power. The fan pumping power is higher for depths larger than the optimum because of higher pressure drop; it is also higher for depths smaller than the optimum because of the smaller heat transfer area and the correspondingly

larger air flow requirement. Figure 4 shows that the fan pumping power can be greatly reduced by increasing the frontal area although this may not be feasible in automotive applications. Ambient temperature is seen to have a significant effect on the ability to reject heat. The fan pumping power can more than double with a mere 5°C increase in ambient temperature from 40°C to 45°C. The stack temperature has a similar effect on heat rejection ability. For the same pumping power (300 W), the frontal area increases by 40% if the stack operates at 80°C rather than at 90°C. Conversely, for the same frontal area ($A/A_{\text{ref}} = 1.25$), the fan pumping power more than doubles, if the stack operates at 80°C rather than at 90°C.

Water Management

We initiated a study to assess the prospect of meeting the 2010 target requiring unassisted start from -20°C to produce 50% of rated power within 30 s while using <5 MJ energy for startup (and previous shutdown). We formulated a dynamic model for water uptake and transport in the membrane and ionomer in the catalyst layers and used it to analyze startup from subfreezing temperatures (N111 membrane, dispersed Pt/C catalysts, graphite bipolar plates, 1,770 W/kg stack specific power). We found that the initial membrane water content (λ , moles of water in one equivalent weight of the perfluorosulfonic acid membrane) is an important parameter that determines whether a successful self-start is possible. There is a critical λ ($\lambda_h = 7.5$ for startup from -20°C) above which self-start is not possible because the product water completely engulfs the catalyst layers with ice before the stack can warm up to 0°C. There is

FIGURE 4. Performance of FCS High Temperature Radiator with 24-fpi Louver Fins

a second value of λ ($\lambda_i = 5$) below which the stack can be self-started without forming ice. Between λ_i and λ_h , the stack can be self-started, but with intermediate formation of ice that melts as the stack warms up to 0°C. Both λ_i and λ_h are functions of the initial stack temperature, cell voltage at startup, membrane thickness, catalyst loading, and stack heat capacity. The higher the initial stack temperature and the lower the cell voltage, the higher are λ_i and λ_h . Our simulations show that the startup from a subfreezing temperature is robust for $\lambda < \lambda_i$, since ice does not form as the membrane absorbs the product water during the time that the stack warms up to 0°C. Startup under this condition results in the current density monotonically increasing with time. During startup for $\lambda_i < \lambda < \lambda_h$, the product water is initially absorbed in the membrane until it becomes locally saturated ($\lambda=14$ for Nafion®) after which ice begins to form. Thus, startup for $\lambda_i < \lambda < \lambda_h$ results in the current density initially increasing with time and then declining with time. All the product water turns into ice if the initial λ is greater than 14 and the current density monotonically decreases with time.

We have also analyzed the time required and the energy consumed during shutdown in order to prepare the stack for a subsequent successful startup from subfreezing temperatures (i.e., to “dry” the stack to $\lambda_i < \lambda < \lambda_h$). We have run simulations to study the drying of the membrane by purging the cathode with air (no anode purge) as a function of the initial stack temperature and water content of the catalyst and gas diffusion layers (saturation levels). We find that, depending on the initial saturation level, it may not be possible to dry the membrane to the target λ if the stack at the start of the purge cycle is below a certain temperature. This points to a potential problem in that a robust start from subfreezing temperature may be difficult if the prior shutdown occurred after a short drive that resulted in the stack being heated to <30–50°C.

Finally, we have determined the optimum λ for robust and rapid startup and shutdown. Startup and shutdown time and energy may be unacceptable if the λ is much less than the optimum. Conversely, a robust startup from subfreezing temperatures cannot be assured if the λ is much higher than this optimum.

Conclusions and Future Directions

- The Honeywell design of the air management system can reach peak component efficiencies of 70.3% for the compressor, 73.2% for the expander, 86% for the motor, and 87.3% for the motor controller. The VNT allows the module to be adapted to different design pressures.
- Even with the reconfigured design that utilizes the cooling air, the air management system consumes about ~9 kWe to deliver 91 g/s air at 2.5 bar

stack inlet pressure for an 80-kWe FCS. Further improvements in aerodynamics are needed to reach the DOE target of no more than 4.4-kW parasitic power.

- We have compared the performance of pressurized and near-ambient pressure FCSs with NSTFCs. We have concluded that in spite of the larger parasitic losses in the air management system and the higher operating cell voltage needed to achieve 50% system efficiency, the Pt content is lower with the pressurized system than with the near ambient pressure system.
- Our analysis of the experimental data for the four types of fins tested on subscale radiators leads us to conclude that the 24-fpi louver fins is the best option from the standpoint of blower pumping power and radiator compactness.
- Initial membrane water content (λ) is an important parameter that determines whether a successful unassisted self-start is possible from subfreezing temperatures. Similarly, the stack temperature prior to shutdown largely determines the time and energy required to dry the membrane to specific values of λ , for which self-start is possible.
- In FY 2010, we will redo the system analysis with reduced Pt loading of 0.1 mg/cm²(c) and 0.05 mg/cm²(a). We will consider catalyst and membrane durability in addition to system cost and performance. Also, we will analyze the dynamic performance of the fuel cell system under real-world driving conditions.

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V.A.2 Mass Production Cost Estimation for Direct H₂ PEM Fuel Cell System for Automotive Applications

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Contract Number: GS-10F-0099J

Project Start Date: February 17, 2006

Project End Date: February 17, 2010

Objectives

1. Identify the lowest cost system design and manufacturing methods for an 80 kW_e direct-H₂ automotive proton exchange membrane (PEM) fuel cell system based on three technology levels:
 - Current status
 - 2010 projected performance
 - 2015 projected performance
2. Determine costs for these three technology level systems at five production rates:
 - 1,000 vehicles per year
 - 30,000 vehicles per year
 - 80,000 vehicles per year
 - 130,000 vehicles per year
 - 500,000 vehicles per year
3. Analyze, quantify and document the impact of fuel cell system performance on cost.
 - Use cost results to guide future component development

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section (3.4.4) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

(B) Cost

Technical Targets

This project will provide realistic, defensible fuel cell power systems cost estimates for comparison with the DOE technical targets. Insights gained from these estimates will help to adjust and further validate the DOE targets. Furthermore, our analysis will shed light on the areas in need of the most improvement and thereby provide guidance for future fuel cell research and development efforts.

TABLE 1. DOE Targets/DTI Estimates (at 500,000 Systems/Year Manufacturing Rate)

Stack Cost, \$/kW _{e (net)}	2005 Status	Current (2006/2007/2008)	2010	2015
DOE Target:	\$65	-	\$25	\$15
DTI 2006 Estimate (Year 1):	-	\$66	\$30	\$25
DTI 2007 Estimate (Year 2):	-	\$50	\$27	\$23
DTI 2008 Estimate (Year 3):	-	\$38	\$29	\$25
System Cost, \$/kW_{e (net)}				
DOE Target:	\$125	-	\$45	\$30
DTI 2006 Estimate (Year 1):	-	\$108	\$70	\$59
DTI 2007 Estimate (Year 2):	-	\$94	\$66	\$53
DTI 2008 Estimate (Year 3):	-	\$72	\$65	\$51

Accomplishments

- Improved existing conceptual design and component specification of complete fuel cell power systems at three technology levels (2008, 2010, and 2015).
- Completed 2008 Status Update Report (2008, 2010, 2015 technologies).

- Performed detailed sensitivity analysis using tornado charts and Monte Carlo techniques.
- Analyzed new technologies and manufacturing alternatives.
- Identified components and systems that warrant further research.

Introduction

In this project, DTI has built on previous analyses to estimate the cost of 80 kW_{e (net)} PEM fuel cell vehicular power systems at five annual production rates (1,000, 30,000, 80,000, 130,000, and 500,000 systems per year) and three levels of projected fuel cell and manufacturing technology (current, 2010, and 2015). During the first year of the project, we investigated the technology and prepared the cost models to reflect 2006, 2010, and 2015 estimates of PEM technology. This annual report covers the third year of the DTI project and focuses on refinement of the cost estimates and an update to reflect 2008 advances in technology.

A Design for Manufacturing and Assembly (DFMA[®]) methodology is employed to obtain the cost estimates. DFMA[®] is a methodology created by Boothroyd Dewhurst Inc. to systematically estimate the manufacturing and assembly costs of a component or system. By analyzing variations in component design and manufacturing methods, one can conduct a comparative cost analysis and determine the pathway to achieving the lowest system cost. Normally, a markup rate is used within the DFMA[®] methodology to reflect the business costs of general and administrative, scrap, research and development (R&D), and profit and is applied to all levels contributing to the effort (original equipment manufacturer, Tier 1, Tier 2, etc.). However, per DOE directive for this project, a markup is only applied to lower-tier supplied materials and components, not to materials or operations conducted by the highest-tier fuel cell assembler. (Scrap costs are included at the component level but not at the system level.)

The costs reported in this document reflect the values from the 2008 status update.

Approach

There are four main steps to our approach: research, system modeling, component design, and application of DFMA[®]-style redesign and costing techniques. The first step, research, has been conducted continuously throughout the project. It encompasses the review of published materials and patents, as well as interviews with key researchers and manufacturers. This provides a common ground assessment of the system layout

and technologies currently used or anticipated to be used by the fuel cell system community. After enough information was collected to move forward, a preliminary system concept and mechanical/piping layout were developed to meet the technical requirements for each of the three different systems to be examined: current, 2010, and 2015 technologies. Excel spreadsheet-based performance models were used to determine heat loads, mass flows, compositions, and pressure levels throughout the systems. The flow diagrams were then iteratively modified to obtain a projected optimal configuration and performance.

Armed with the preliminary system concepts and layouts, we designed each of the main components that make up the system. This involved specifying the detailed geometries of the flow plates, gaskets, membrane electrode assemblies (MEAs), etc., and determining which materials to use. The most appropriate manufacturing processes to use for each component were then selected based primarily on cost, but with consideration of the performance and durability parameters. Several different cases were analyzed when it was unclear which approach was best, and the component designs were adjusted to suit the manufacturing method. For each component, we defined a manufacturing process train, and then applied our costing methodologies to it. Using a comprehensive DFMA[®]-style approach, we calculated the manufacturing process costs, setup costs, material costs, and assembly costs, and then summed them to determine the total costs for the stack and the system. Amortization of the machinery capital costs and expendable tooling, as well as labor costs (including indirect labor costs for fringe benefits) were included in the cost estimates. The costs of some non-stack components such as radiators, pumps, blowers, controllers, sensors, etc. were calculated by a simplified DFMA[®]-style methodology, or were based on price quotations from vendors.

Results

The cost differences across the three different technology levels (see Table 2 and Figure 1) were driven primarily by expected improvements in stack power density (715 to 1,000 mW/cm²), total platinum loading (0.25 to 0.2 mgPt/cm²), operating pressure (2.3 to 1.5 atm), and peak stack temperature (90 to 120°C). Stack cost reductions primarily resulted from increased power density and decreased platinum loading. Balance-of-plant (BOP) cost reductions stemmed primarily from system simplifications (i.e. reduced or eliminate components). For example, the current technology system uses water spray injection for the air humidification, the 2010 system uses a polyamide membrane humidification system, and the 2015 has no air humidification system at all. Simplifications of

TABLE 2. System Comparison

	2008 Technology System	2010 Technology System	2015 Technology System
Power Density (mW/cm ²)	715	1000	1000
Total Pt loading (mgPt/cm ²)	0.25	0.3	0.2
Operating Pressure (atm)	2.3	2	1.5
Peak Stack Temp. (°C)	70-90	99	120
Membrane Material	Nafion on ePTFE	Advanced High-Temperature Membrane	Advanced High-Temperature Membrane
Radiator/Cooling System	Aluminum Radiator, Water/Glycol coolant, DI filter	Smaller Aluminum Radiator, Water/Glycol coolant, DI filter	Smaller Aluminum Radiator, Water/Glycol coolant, DI filter
Bipolar Plates	Stamped SS 316L with Coating	Stamped SS 316L with Coating	Stamped SS 316L with Coating
Air Compression	Twin Lobe Compressor, Twin Lobe Expander	Centrifugal Compressor, Radial Inflow Expander	Centrifugal Compressor, No Expander
Gas Diffusion Layers	Carbon Paper Macroporous Layer with Microporous layer applied on top	Carbon Paper Macroporous Layer with Microporous layer applied on top	Carbon Paper Macroporous Layer with Microporous layer applied on top
Catalyst Application	Double-sided vertical die-slot coating of membrane	Double-sided vertical die-slot coating of membrane	Double-sided vertical die-slot coating of membrane
Air Humidification	Water spray injection	Polyamide Membrane	None
H ₂ Humidification	None	None	None
Exhaust Water Recovery	SS Condenser (Liquid/Gas HX)	SS Condenser (Liquid/Gas HX)	None
MEA Containment	Injection molded LIM Hydrocarbon MEA	Injection molded LIM Hydrocarbon MEA	Injection molded LIM Hydrocarbon MEA
Coolant & End Gaskets	Laser Welding/Screen Printed Resin	Laser Welding/Screen Printed Resin	Laser Welding/Screen Printed Resin
Freeze Protection	Drain water at shutdown	Drain water at shutdown	Drain water at shutdown
H ₂ Sensors	2 H ₂ sensors (for FC sys), 1 H ₂ sensor (for passenger cabin; not in cost estimate), 1 H ₂ sensor (for fuel sys; not in cost estimate)	1 H ₂ sensor (for FC sys), 1 H ₂ sensor (for passenger cabin; not in cost estimate), 1 H ₂ sensor (for fuel sys; not in cost estimate)	No H ₂ sensors
End Plates/Compression System	Composite molded end plates with compression bands	Composite molded end plates with compression bands	Composite molded end plates with compression bands
Stack/System Conditioning	5 hours of power conditioning	4 hours of power conditioning	3 hours of power conditioning

the air, humidification, and coolant systems yielded the majority of technology improvement savings.

The stack cost decreases with advancing technology level due to both power density improvement and gross power reduction. Major cost reductions are not currently projected as a result of manufacturing method change or material selection. Rather, future improvements in stack power density (as a result of expected improved MEA performance) results in the cells shrinking geometrically and thereby incurring less material cost. Additionally, gross power requirements (ranging from 90.3 to 87.1 kW_e) are directly driven by

the aforementioned BOP component selection (specifically, the differing air compression approaches), and lead to further cell size and cost reduction.

Unsurprisingly, the stack cost is the largest and most important contributor to the system cost. While most of the BOP components are based on modifications of proven, existing technology, the stack designs are comparatively immature. The impact of this is twofold: the stack has the most room for technological improvement and the component production methods are less defined. Therefore, most of our analysis is focused on the stack, since it provides the most potential for cost improvement.

One of the key changes for the 2008 update (compared to the 2007 estimate) is in selection of the power density and platinum loading levels. High power density generally correlates with high Pt loading thus a careful optimization must be conducted to achieve the lowest cost design point. Based on 2008 estimates of performance, the power density and platinum loading design point was re-optimized to 715 mW/cm² at 0.25 mg Pt/cm² (2008 status) from the previous 583 mW/cm² at 0.3 mg Pt/cm² (2007 status). (Design points for 2010 and 2015 remain unchanged.) Decreasing the platinum loading resulted in a major cost reduction (\$9.81/kW) and increasing the power density resulted in another significant cost decrease (\$7.17/kW). The net effect of these two changes is a \$16.98/kW cost reduction, which represents the majority of the \$18.51 drop in system cost from 2007 status levels.

Though no other change had as much impact as those two, a variety of other important changes helped to further reduce the system cost, and many of them did so for all three technology levels. By switching to laser-welded coolant gaskets and screen-printed end gaskets, another \$4.06/kW was saved. Halving the number of system controllers (from two to one) cut \$2.50/kW from the cost, and adjusting the labor rate from \$60/hr to \$45/hr dropped it another \$1.24/kW. However there were also a few changes which increased cost, such as

FIGURE 1. Stack Cost Component Distribution

updating material and machinery prices (\$1.92/kW), and the addition of a coating on the stamped metal bipolar plates (\$1.77/kW). Because the 2010 and 2015 systems did not benefit from the same improvements in power density and catalyst loading as the current technology did, stack cost projections actually went up for those two systems. Fortunately cost savings from the BOP components were able to compensate for these increases, so the overall system costs went down for all three systems (as compared to the 2007 analysis).

Numerous other minor assumption changes were made, the result of which yields a small cumulative net savings: while their net effect is comparatively small, the improvements improve the analysis appreciably and lead to greater confidence in the cost estimates.

At 500,000 systems per year, the total cost for the stacks, including assembly and stack conditioning, comes to \$38/kW_{net}, \$29/kW_{net}, and \$25/kW_{net}, for the 2008, 2010, and 2015 technology year cost projections, respectively (see Figure 2). These should be compared to the 2010 and 2015 DOE stack targets of \$25/kW_{net} and \$15/kW_{net}. When accounting for the BOP items, the system costs are roughly double that of the stacks alone and sum to \$75/kW_{net}, \$62/kW_{net}, and \$51/kW_{net}

FIGURE 2. Stack Cost in \$/kW_{net}

for 2008, 2010, and 2015, respectively, all at 500,000 systems per year (see Figure 3).

Note that platinum cost is held constant at \$1,100 per troy ounce to allow direct comparison with previous estimates. System cost is highly dependent on this

FIGURE 3. System Cost in $\$/kW_{e(net)}$

assumption, especially for the current technology system, which has a relatively high Pt loading and low power density. In recent months, the platinum prices have returned to roughly \$1,150 per troy ounce, which validates the \$1,100 used. However, if prices were to return to their 2008 peak of \$2,280 per troy ounce, the stack costs would leap by \$16, \$13, and \$9 per kW_{net} for the three different technology levels, respectively. Sensitivity analysis tornado charts for the 2008 and 2015 system cost are shown in Figure 4.

FIGURE 4. System Cost Sensitivity Analysis

Conclusions and Future Directions

Key conclusions from the second year of the project include:

- All cost estimates were recomputed to reflect 2008 technology advances and an overall improvement in modeling methods.
- This cost estimate update results in across-the-board cost reductions with the largest savings occurring between the 2007 status estimate and the 2008 status estimate.
- 2010 and 2015 stack cost estimates (at 500,000 systems/year) are predicted to be \$4/kW and \$10/kW higher than DOE targets, respectively.
- 2010 and 2015 system cost estimates (at 500,000 systems/year) are predicted to be \$17/kW and \$21/kW higher than DOE target, respectively.
- Significant technical breakthroughs will be required in order to achieve the 2010 and 2015 DOE system cost targets.
- Catalyst cost (especially platinum) is the largest single cost contributor, so any efforts to reduce the amount used will yield large savings.
- Substantial cost reductions (factors of 3-5) are achieved by increasing manufacturing volume from 1,000 to 500,000 systems per year production rate.
- BOP components are comparable to stack costs. Consequently, R&D to reduce, simplify, or eliminate BOP components is needed to achieve a significant overall system cost reduction.
- Most of the BOP cost reduction that is expected to occur as technology level advances occurs from simplification of the air compressor, humidification, and hydrogen sensor subsystems. R&D is needed to ensure that these projected advances are achieved.

When compared to the DOE's 2005 status values and our 2006 and 2007 estimates from the previous two years, it's clear that the significant technology advances of the last several years have resulted in substantial cost

reductions. Still, there is a substantial predicted overage in meeting 2010 targets: \$4/kW on the stack and \$17/kW for the system. The expected overage for 2015 grows to \$10/kW and \$21/kW for the stack and system respectively. Further R&D or system configuration advances are needed to close these gaps.

On such potential advance is the development of the nano-structured thin-film catalyst application technology, developed by 3M. They have recently demonstrated a platinum catalyst loading and areal power density pairing of 815 mW/cm² and 0.15 mg/cm², which surpasses the DOE's 2010 targets and could help to dramatically lower the fuel cell system cost. In the 2009 analysis, DTI will examine this technology and integrate it as an option in our cost analysis.

Additionally, DTI will address the following topics:

- Updating the 2008 technology system to reflect 2009 technology.
- A detailed bottom-up DFMA[®] analysis of Honeywell turbochargers.
- Optimization of the power density-catalyst loading design point.
- Alternative catalyst alloys.
- Examination of low-pressure fuel cell systems.
- Additional sensitivity analysis.

FY 2009 Publications/Presentations

1. September 18th, 2008 – Washington, D.C.: Status Presentation at DOE Headquarters.
2. September 24th, 2008 - [Videoconference]: Presentation to Fuel Cell Tech Team.
3. December 4th, 2008 – [Videoconference]: Presentation to Independent Review Panel.
4. May 21st, 2009 - Crystal City, VA: DOE H₂ Program Review Presentation.
5. July 15th, 2009 - Hartford, CT: HTAC Open Meeting.

V.A.3 Cost Analyses of Fuel Cell Stacks/Systems

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Contract Number: GS-23F-0064L

Order Number: DE-AD36-06GO26044

Project Start Date: February 17, 2006
Project End Date: February 16, 2010 (Option
Year 2)

Objectives

The overall objective is to assess the high-volume (500,000 units/year) manufacturing cost for an 80 kW (net) direct-hydrogen polymer electrolyte membrane fuel cell (PEMFC) system for automotive applications. This past year's (2008-2009) objectives were:

- Estimate the bottom-up manufactured cost of the 2008 PEMFC system, assuming a nano-structured thin film catalyst (NSTFC)-based membrane electrode assembly (MEA) and a 30 micron perfluorosulfonic acid (PFSA) membrane.
- Perform sensitivity analyses on key stack and system parameters, assuming high-volume production (500,000 units/year) of the 2008 PEMFC system.
- Participate in an independent peer review of our 2008 cost analysis methodology, assumptions, and resulting cost projections.
- Update the bottom-up manufactured cost for the PEMFC system based on updated stack performance assumptions and system configuration for 2009.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section (3.4.4) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

(B) Cost

Technical Targets

This project evaluates the cost of automotive PEMFC technologies being developed by DOE contractors and other developers. Insights gained from this evaluation will help guide DOE and developers toward promising stack and system-level designs and approaches that could ultimately meet the DOE targets for PEMFC system cost, specific power, power density, and efficiency. DOE cost targets and current high-volume cost estimates based on the 2008 system configuration are shown in Table 1.

Accomplishments

- Updated the bottom-up manufacturing cost for the 2008 PEMFC system configuration assuming current technology status and high-volume production (500,000 units/year).
- Performed single-variable and multi-variable (Monte Carlo) sensitivity analyses on key stack and system parameters for high-volume production (500,000 units/year).
- Participated in an independent peer review of our 2008 cost analysis methodology, assumptions, and resulting cost projections.
- Developed preliminary bottom-up, high-volume manufacturing cost estimate for the 2009 PEMFC stack, assuming current technology status.

Introduction

The DOE seeks to develop a durable fuel cell power system for transportation applications. Cost is a major challenge to the commercialization of automotive fuel cell power systems. The cost of fuel cell power systems must be reduced to less than \$50/kW for the technology to be competitive with automotive internal combustion engine power plants, which currently cost about \$25-35/kW.

TABLE 1. Progress towards Meeting Cost Targets for PEMFC Systems for Transportation Applications

Component	Cost Units	DOE 2010/2015 Targets	DOE 2008/2009 Targets	TIAX 2008 Status	Comments
System	\$/kW _e	45/30	70/60	57	Based on bottom-up manufacturing cost and an assumed 15% markup to the automotive original equipment manufacturer (OEM) for all major balance-of-plant (BOP) components
Stack	\$/kW _e	25/15		29	Based on bottom-up manufacturing cost and assumes no markup for all major stack components
Compressor Expander Motor (CEM)	\$/unit	400/200		615	Assumes 15% markup to the automotive OEM
Membrane	\$/m ²	20/20		16	
Electrocatalyst	\$/kW _e	5/3		16	
MEA	\$/kW _e	10/5		20	
Bipolar Plates	\$/kW _e	5/3		3	

A rigorous, bottom-up analysis of projected high-volume manufacturing cost is required to accurately gauge the status and potential of fuel cell technology to meet the FreedomCAR and Fuel Partnership goals. TIAX LLC (formerly the Technology and Innovation group within Arthur D. Little) has assisted DOE with the development of cost projections for PEMFCs for transportation since 1999, analyzing reformat-based systems through 2004, followed by direct-hydrogen systems from 2005 through 2009.

Approach

We have applied an internally developed technology-costing methodology that has been customized to accurately analyze and quantify the processes used in the manufacture of PEMFC stack as well as BOP components. TIAX has developed a proprietary, bottom-up, technology-based cost model which is used in conjunction with the conventional Boothroyd-Dewhurst Design for Manufacturing and Assembly (DFMA[®]) software.

The approach starts with a technology assessment of the system configuration and components. We perform a literature and patent search to explicate the component parts, specifications, material type, and manufacturing process. Subsequently for each component, we develop a bill of materials based on the system specification/performance modeling provided by Argonne National Laboratory (ANL), determine material costs at the assumed production volume, break down manufacturing processes into unit operations, and identify appropriate manufacturing equipment. We also perform single-variable and multi-variable (Monte Carlo) sensitivity analyses to identify the major cost drivers and the impact of material price and process assumptions on the high-volume PEMFC system cost results.

Finally, we solicit feedback from the Fuel Cell Tech Team, developers and vendors on the key performance assumptions, process parameters, and material cost assumptions; we calibrate our model using this feedback.

Results

Throughout this document, we report a “factory cost”, which is a bottom-up estimate of the high-volume manufacturing cost based on an 80 kW net power PEMFC system, and an “OEM cost”, which assumes a 15% markup (over the factory cost) to the automotive OEM for the BOP components. We assumed a vertically integrated process for the manufacture of the PEMFC stack by the automotive OEM, so no markup is included on the major stack components. Raw materials and purchased components implicitly include supplier markup.

In 2007, the PEMFC system configuration, materials, processes, performance assumptions, and component specifications were updated [1,2]. We developed bottom-up manufacturing cost models for both stack and BOP components [1,2]. During the current reporting period (2008-2009), we updated key stack performance assumptions, i.e. power density and platinum (Pt) loading, with no change to the system layout, cell voltage, or stack operating conditions, i.e. no change to stack efficiency [3-5]. We based our cost assessment on ANL's single-cell modeling which is calibrated using data from an NSTFC-based short stack. We assumed a baseline Pt cost of \$1,100/tr.oz., and captured the variability in Pt cost through the lower and upper bounds of the sensitivity analyses.

Table 2 is a summary of stack performance assumptions in 2005, 2007, and 2008.

TABLE 2. Key Stack Performance Assumptions

Parameters	Units	2005 [6]	2007 [1,2]	2008 [3-5]
System net power	kW _e	80	80	80
Stack gross power	kW _e	89.5	86.4	86.9
Stack gross power density	mW/cm ²	600	753	716
Cell voltage (rated power)	V	0.65	0.68	0.685
Pt loading (total)	mg/cm ²	0.75	0.30	0.25
Membrane thickness	μm	50	30	30
Stack temperature	°C	80	90	90
Pressure (rated power)	atm	2.5	2.5	2.5
Stack efficiency (rated power)	% LHV	52%	54%	54%

LHV – lower heating value

Overall, the 2008 assumptions lowered the stack cost by ~57% to \$29/kW [3-5] and the system cost by ~47% to \$57/kW [3-5] over the 2005 estimates [6] due to a significant reduction in Pt loading with increase in power density and the use of bottom-up methodology for estimating high-volume cost of BOP components. The lower Pt loading is attributed to novel catalyst and support structure (i.e. NSTFC on organic whisker support). Material costs dominate the high-volume factory cost of the PEMFC stack components. Pt material cost alone makes up ~90% of the electrode cost, while the electrodes represent ~54% of the \$29/kW stack cost. Therefore, Pt cost accounts for ~48% of the total stack cost.

Because there were no changes to the assumed BOP subsystems in 2008, their high-volume factory cost of \$1,350 (OEM cost of \$1,500) is unchanged from 2007 [1,2]. The projected compressor expander motor factory cost of \$535 or ~\$7/kW is the largest contributor to the combined BOP and assembly cost of \$28/kW [3-5].

Figure 1 shows the breakdown of the 2008 PEMFC stack and system cost by component and subsystem, respectively. Both stack and BOP component costs are significantly reduced from the 2005 cost assessment [6]. With the much reduced stack cost of \$29/kW in 2008, BOP and assembly together represent ~50% of the PEMFC system cost in 2008, compared to ~38% in 2005 [3-5].

We performed single- and multi-variable sensitivity analyses to examine the impact of major stack and BOP parameters on the high-volume 2008 PEMFC system

¹ High-volume manufactured cost based on a 80 kW net power PEMFC system. Does not represent how costs would scale with power (kW).

² Assumes 15% markup to the automotive OEM for BOP components.

FIGURE 1. 2008 PEMFC Stack and System Cost [5]

cost. As seen in Figure 2, Pt loading, power density, and Pt cost are the top three drivers of the PEMFC system OEM cost. The results of a multi-variable (Monte Carlo) analysis are shown in Figure 3; the high-volume 2008 PEMFC system OEM cost ranges between \$45/kW and \$101/kW ($\pm 2\sigma$), with the mean of the distribution being \$73/kW [5].

FIGURE 2. 2008 Stack Single-Variable Sensitivity Analysis [5]

¹ High-volume manufactured cost based on a 80 kW net power PEMFC system. Does not represent how costs would scale with power (kW).
² Assumes 15% markup to the automotive OEM for BOP components.

FIGURE 3. 2008 System Multi-Variable (Monte-Carlo) Analysis [5]

We are currently working with DOE and ANL to define the 2009 system configuration, update stack performance assumptions, system parasitics and BOP component specifications. Figure 4 shows a preliminary layout of the 2009 PEMFC system [5,7,8]. The key changes proposed over the 2008 configuration [3,4] are: the enthalpy wheel humidifier (EWH) will be replaced by a planar membrane humidifier (MH) with precooler for cathode air humidification; tubular MH for anode hydrogen humidification will be replaced by a planar MH; and the low-temperature (LT) radiator, LT coolant pump for air precooler, and needle metering valve for CEM will be included in the scope of the 2009 PEMFC system [5,7,8].

Our preliminary estimates show that the high-volume 2009 PEMFC stack cost for three scenarios ranges between \$24/kW to \$33/kW [5], based on initial results from ANL's stack and system modeling [7,8]. Table 3 outlines the key assumptions and cost of the three stack scenarios modeled in 2009 [5]. All scenarios assume a Pt cost of \$1,100/tr.oz., NSTFC-based MEA, 30 μm PFSA membrane, and stack operating conditions of 90°C and 2.5 atm.

Using the 2008 estimate of \$28/kW for the BOP and assembly cost [3,4], the preliminary 2009 PEMFC system OEM cost is estimated to range between \$52/kW to \$61/kW. These initial estimates will be finalized by the next reporting period.

FIGURE 4. Preliminary 2009 PEMFC System Configuration [7,8]

TABLE 3. Preliminary 2009 PEMFC Stack Scenarios

Parameters	Units	2009 Stack Scenarios [5]		
		S1	S2	S3
System net power	kW_e	80		
Stack gross power	kW_e	91.6	92.0	92.5
Cell voltage (rated power)	V	0.721	0.685	0.655
Stack gross power density	mW/cm^2	640	837	966
Pt loading (total)	mg/cm^2	0.25		
Stack efficiency (rated power)	% LHV	57.4%	54.5%	52.1%
System efficiency (rated power)	% LHV	50.0%	47.3%	45.0%
System voltage (rated power)	V	300		
System Active area	m^2	14.3	11.0	9.6
Stack cost	$\\$/\text{kW}_{\text{net}}$	33	26	24

Conclusions and Future Directions

- Both stack and BOP component costs are significantly reduced from the 2005 cost assessment. The 2008 PEMFC stack cost of \$29/kW is ~57% lower than the 2005 stack cost [6] due to a

significant reduction in Pt loading with increase in power density. The lower Pt loading is attributed to novel catalyst and support structure (i.e. NSTFC on organic whisker support). The 2008 PEMFC system cost of \$57/kW is ~47% lower than the 2005 system cost [6] due to the use of bottom-up methodology for estimating high-volume cost of BOP components.

- With the much reduced stack cost of \$29/kW in 2008, BOP and assembly together represent ~50% of the PEMFC system cost in 2008, compared to ~38% in 2005 [6].
- The CEM factory cost (without supplier markup) of approximately \$7/kW is the largest contributor to the overall BOP cost [3-5].
- Platinum loading, power density, platinum cost, membrane cost and CEM cost are the top five drivers of the PEMFC system cost [5].
- The 2008 stack and system costs of \$29/kW and \$57/kW are ~15-30% higher than the DOE 2010 targets of \$25/kW and \$45/kW, respectively [3-5].
- Preliminary estimates for the high-volume 2009 PEMFC stack cost range between \$24/kW and \$33/kW for different stack scenarios. These initial estimates will be finalized by the next reporting period [5].

Our next steps are outlined below:

- Complete a comprehensive report on the 2008 PEMFC cost analysis (high-volume, bottom-up stack and BOP cost).
- Seek feedback from key developers, vendors and the Fuel Cell Tech Team on performance assumptions and cost analysis and incorporate any modifications.
- Finalize 2009 PEMFC system layout and performance assumptions. Update cost results for 2009 based on input from ANL, on-going development and testing of state-of-the-art PEMFC stacks and systems.

FY 2009 Publications/Presentations

1. *Direct Hydrogen PEMFC Manufacturing Cost Estimation for Automotive Applications*, J. Sinha, S. Lasher, Y. Yang, DOE Annual Merit Review, Arlington, VA, May 21, 2009.

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1. *Direct Hydrogen PEMFC Manufacturing Cost Estimation for Automotive Applications*, S. Lasher, J. Sinha, Y. Yang and S. Sriramulu, DOE Annual Merit Review, Washington, D.C., May 18, 2007.
2. *Cost Analyses of Fuel Cell Stacks/Systems*, S. Lasher, J. Sinha and Y. Yang, DOE Hydrogen Program Annual Report, V.A.5, 2007.

3. *Direct Hydrogen PEMFC Manufacturing Cost Estimation for Automotive Applications*, J. Sinha, S. Lasher, Y. Yang and P. Kopf, DOE Annual Merit Review, Washington, D.C., June 10, 2008.

4. *Cost Analyses of Fuel Cell Stacks/Systems*, J. Sinha, S. Lasher and Y. Yang, DOE Hydrogen Program Annual Report, V.A.3, 2008.

5. *Direct Hydrogen PEMFC Manufacturing Cost Estimation for Automotive Applications*, J. Sinha, S. Lasher, Y. Yang, DOE Annual Merit Review, Arlington, VA, May 21, 2009.

6. *Cost Analysis of PEM Fuel Cell Systems for Transportation*, E.J. Carlson, P. Kopf, J. Sinha, S. Sriramulu and Y. Yang, NREL Report - NREL/SR-560-39104, September 30, 2005.

7. *Status of Automotive Fuel Cell Systems*, R.K. Ahluwalia and X. Wang, internal communications, March 3 & May 10, 2009.

8. *Fuel Cell Systems Analysis*, R.K. Ahluwalia, X. Wang, K. Tajiri and R. Kumar, DOE Annual Merit Review, Arlington, VA, May 21, 2009.

V.A.4 Fuel Cell Testing at Argonne National Laboratory

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Start Date: 1996
Projected End Date: Project continuation and
direction determined annually by DOE

We are testing stacks from different developers and documenting their performance according to well-defined test protocols for comparison of the measured performance against DOE targets.
Milestone 87: Test and evaluate fuel cell systems and components such as MEAs, short stacks, bipolar plates, catalysts, membranes, etc., and compare to targets. (1Q, 2011)

We are testing fuel cell stacks, balance-of-plant components, and complete systems to document their performance for comparison to DOE targets.

- *Milestone 88: Test and evaluate fuel cell systems and components such as MEAs, short stacks, bipolar plates, catalysts, membranes, etc., and compare to targets. (4Q, 2015)*

We are testing fuel cell stacks, balance-of-plant components, and complete systems to document their performance for comparison to DOE targets.

Objectives

- Provide DOE with an independent assessment of the performance of fuel cell systems and components developed under DOE contracts.
- Characterize and benchmark the performance of state-of-the-art commercial fuel cell technology available in the market.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section (3.4) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) Durability
- (C) Performance
- (D) Water Transport within the Stack
- (G) Start-up and Shut-down Time and Energy/Transient Operation

Contribution to Achievement of DOE Fuel Cells Milestones

This project will contribute to achievement of the following DOE milestones from the Fuel Cells section of the Hydrogen, Fuel Cells, and Infrastructure Technologies Program Multi-Year Research, Development, and Demonstration Plan:

- *Milestone 86: Evaluate short stack against 2011 targets for operation over the full operating temperature range. (4Q, 2010)*

Accomplishments

- Characterized one 5-kW complete system.
- Participated in and made technical presentations at the third and fourth meetings of the International Organization for Standardization Working Group 11 under Technical Committee 105 of the International Electrotechnical Commission, held on October 13-14, 2008, in Pusan, Korea, and on April 6-7, 2009, in Vancouver, BC, Canada, respectively. The goal of this international group is to draft the technical specification of a single-cell test protocol. Representatives from six countries attended.
- Began collaborative effort to compare the test protocols developed by the European FCTESTNET/FCES^{QA} and by DOE. The objective of the effort is to determine if there are significant differences in the procedures used to characterize the performance of fuel cell stacks and to age the stacks.

Introduction

This project helps DOE determine and document progress toward achieving its technical targets by providing an independent assessment of evolving fuel cell technology. In addition, in this project we develop standard fuel cell testing procedures to aid in the evaluation of different stack technologies. The procedures and methods used are transparent to the technology being tested; thus, they provide a means for easy comparison of the performance and expected life of the technology from many different developers. In

these procedures, the stack is characterized in terms of initial performance, durability, and low-temperature performance. To further accelerate fuel cell technology developments, these procedures are compared with similar procedures developed by other national and international organizations.

The initial performance establishes a baseline for comparison as the fuel cell ages. The aging process is accelerated to yield a reasonable projection of life at constant power and under driving duty cycles in a reasonable amount of testing time. Periodically during the aging test, the test is interrupted and the stack performance is re-characterized. A life projection is then made by comparing the most recent performance characteristics with those measured earlier.

Approach

We have developed standardized fuel cell and stack test procedures to aid in the evaluation of different stack technologies. These test procedures characterize the stack in terms of initial performance (e.g., power and voltage vs. current, efficiency, hydrogen cross-over), durability, and low-temperature performance. The testing is repeated during and after defined aging under steady-state and cycling operations to determine performance decay over time.

The test facility is flexible enough to accommodate the unique needs of different technologies. Modification and upgrading of the test facility is an ongoing process that is carried out in consultation with fuel cell developers and DOE.

Results

The performance of a 5-kW, direct hydrogen fuel cell system was characterized in terms of polarization behavior (sequential and random polarization curves) of the fuel cell stack. For these tests, the system was cycled using the dynamic stress test (DST) profile shown in Figure 1 to simulate accelerated aging of the stack. The DST profile consists of several steps, representing different current levels ranging from 0 A to current values where the average cell voltage in the stack is 0.6 V/cell. After every ~100 h of this accelerated aging protocol, the DST cycling was stopped and the stack performance was characterized by measuring a sequential polarization curve.

The stack-only polarization data from this accelerated aging test are shown in Figure 2. The initial performance was in very good agreement with the rated performance of the stack. Further, the data in Figure 2 indicate that there was very little change in the performance of the stack over the first about 1,100 h of the accelerated aging under the DST cycling conditions.

FIGURE 1. Dynamic Stress Test Profile used for Cycling Tests

FIGURE 2. Polarization data from the aging experiment. The curves RPT0 to RPT12 represent polarization data taken after every ~100 h of operation with cycling according to the DST test profile. There were 40 cells in the stack.

After that, however, there was a significant decrease in the measured performance of the stack.

The stability of the stack voltage under load was then measured by running a constant power test at 25% of rated power for 120 h (Figure 3). These data indicate that under these conditions, there was a degradation of stack potential with time at a rate of approximately 16 mV/h.

There is interest in the U.S. and in the European Union (EU) to standardize testing protocols. It is hoped that, with standardized protocols, fuel cell development will be accelerated and information exchange will be increased. Under the FCTESTNET framework program, the EU has developed a set of protocols it is proposing as standards. These protocols are being validated under the FCTES^{QA} program.

As part of the collaboration with FCTES^{QA}, we compared the performance of a hydrogen-fueled, 15-kW stack using the sequential polarization protocols

FIGURE 3. Plot of stack voltage vs. time during constant power test. The apparent oscillations in the voltage trace are due to peripherals (pumps, valves, etc.) switching on and off.

FIGURE 5. Comparison of polarization data obtained using the two protocols.

FIGURE 4. Sequence of current levels used in the polarization protocols developed by DOE and by FC TESTNET.

developed by FC TESTNET and by DOE. The major differences between the two are the sequence of currents used and the portion of the polarization experiment that is reported as the polarization curve. Figure 4 shows that the DOE protocol starts at open circuit then increases and decreases the current. The FC TESTNET protocol, on the other hand, starts at about 50% of the rated current then increases, decreases and finally

increases the current. The DOE protocol uses both current increasing and decreasing sections; that from FC TESTNET, only the current-decreasing portion is reported. Figure 5 shows the current-decreasing portion of the polarization curves obtained using the two protocols. There was no significant difference between the two. The observed difference between the curves is within the range of experimental error.

Conclusions and Future Directions

- Continue to characterize DOE fuel cell contract deliverables.
- Continue to benchmark other fuel cell technologies.
- Continue to collaborate with other fuel cell testing laboratories, such as the Institute for Energy (Netherlands), and FC TESTNET^{QA}.
- Continue to work with Working Group 11 to draft the technical specification for a single-cell test protocol.
- Continue to upgrade the test facility by installing new test hardware and software and increasing the temperature and pressure limits of the cooling system.

V.A.5 Component Benchmarking – Subtask Reported: USFCC Durability Protocol Development and Technical-Assisted Industrial and University Partners

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Project Start Date: October 2003
Project End Date: Project continuation and
direction determined annually by DOE

Objectives

- Technically assist fuel cell component and system developers.
- Test and characterize materials and components and provide feedback to developers.
- Validate and compare single cell test protocols (Japan Automobile Research Institute [JARI], European Union [EU], Korea, China).
- Provide support to the U.S. Council for Automotive Research (USCAR), and the USCAR/DOE Freedom Cooperative Automotive Research (FreedomCAR) Fuel Cell Technology Team.
- Review, comment, and refine testing protocols as necessary.
- Validate technical findings as directed by DOE.

Technical Barriers

This project can be directed to address any of technical barriers from the Fuel Cells section (3.4.4.2) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan, however it principally addresses:

- (A) Durability
- (B) Cost
- (C) Performance

Technical Targets

In this particular task, any of the technical targets in Table 3.4.4, Technical Targets: Integrated Stationary PEM Fuel Cell Power Systems (5-250kW) Operating on Reformate (page 3.4-16 of the Fuel Cells section of the Multi-Year Program Plan; http://www1.eere.energy.gov/hydrogenandfuelcells/mypp/pdfs/fuel_cells.pdf) may be addressed at any given time. Specifically, select tasks that apply to the technical targets in this project are listed below, while their status is listed in the 'Accomplishment' section.

- Provide test insight and advice to DOE solicitation winners.
- Testing and characterization of materials and participation in the further development and validation of a single cell test protocols with the U.S. Fuel Cell Council (USFCC).
- Offering technical assistance to USCAR and the FreedomCAR Fuel Cell Technology Team.
- Supply technical experts to the Tech Team as questions arise, focused single cell testing to support the development of targets and test protocols.
- Participating in working groups and review meetings.

Approach

Our approach has consistently focused on collaborative-type interactions to support the DOE Fuel Cell program. A large portion of this effort goes unpublished, for proprietary reasons. In this fiscal year, we continued testing support and have added several new analytical instruments to an already extensive infrastructure. These addition capabilities include 3-dimensional X-ray tomography, environmental scanning electron microscopy, inductively couple plasma mass spectrometry and mercury intrusion porosimetry. These instruments have been installed and have significantly strengthened our technical-assisting capabilities.

Accomplishments

- Honored several invited presentations.
- Hosted numerous visitors to LANL.
- Collaborated with multiple industrial, university, or laboratory partners.

- Provided testing insight and/or results to several DOE solicitation winners.
- Participated in the review and development of USFCC durability protocols.
- Prepared and tested three 50 cm² fuel cells using LANL's membrane electrode assembly (MEA) fabrication for a comparing JARI, EU and USFCC/ LANL test protocols.
- Held hands-on fuel cell training short-courses

Highlights

Below are some highlights of the technical assistance task for Fiscal Year 2009.

As requested by DOE, LANL tested MEA performance for a funded DOE project at Case Western Reserve University (CWRU, see Figure 1). Performance polarization measurements were made under different conditions to evaluate the performance of MEAs for this project.

During the Nuvera Freeze workshop, scientists from LANL chaired breakout sessions. They openly discussed some of the challenges associated with the impact of freeze/thaw cycling on fuel cell performance. The cyclic voltammograms (CVs) in Figure 2 were taken after cycling the fuel cell from -10°C.

LANL evaluated samples from the National Institute of Standards and Technology (NIST). Figure 3 shows voltammetry examining the anode catalyst provided by NIST.

FIGURE 1. Polarization curves taken at different condition for a commercially available MEA. These results were disseminated to CWRU.

FIGURE 2. Los Alamos demonstrated loss in cathode catalyst surface area with repeated isothermal cold starts at sub-freezing temperatures. This loss was a function of MEA preparation method. These results were openly discussed at the Nuvera Freeze Workshop.

FIGURE 3. Cyclic voltammetry was run on a sample provide by NIST before running subsequent experiments such as hydrogen crossover measurements, break-in procedure, and polarization curves.

FY 2009 Publications/Presentations

1. Garzon, Fernando, Fuel and Air Impurity Effects in Fuel Cells, Gordon Conference, January 2009.
2. Mukundan, Rangachary, Performance and Durability of PEM Fuel Cell at Sub-Freezing Temperatures, Nuvera Freeze Workshop, February 2009.
3. Rockward, Tommy, FreedomCAR Tech Team Update, Detroit, MI, June 2009.

V.A.6 Applied Science for Electrode Cost, Performance, and Durability

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Project End Date: Project continuation and
direction determined annually by DOE

Objectives

- Explore impact of solvent choice in catalyst ink on fuel cell performance.
- Relate the structural and chemical properties of the ionomer in different inks to electrode performance and structure.
- Initiate use of bilayer/gradient structures in electrodes.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) Durability
- (B) Cost
- (C) Performance

Technical Targets

This project engages in studies that enable cost, performance and durability improvements for electrodes, by addressing electrode processes and design criteria that are poorly defined. In Fiscal Year 2009, the structure

and chemical properties of fuel cell ink components were related to performance and durability of the final electrode structure. Insights gained from these studies will be applied toward the design and synthesis of fuel cell materials that meet the following DOE 2010 targets (Tables 3.4.4 and 3.4.12):

- Precious metal loading: 0.3 g/kW
- Cost: \$25/kWe
- Durability with cycling: 5,000 hours

Accomplishments

- Explored wide range of solvents in catalyst inks used to fabricate electrodes; observed marked effect on fuel cell performance.
- Examined structure and local chemical environment of Nafion[®] dispersed in different solvents by neutron scattering and nuclear magnetic resonance (NMR), and related the results to fuel cell performance.
- Demonstrated that solvent choice in catalyst inks has an impact on durability.
- Used transmission electron microscopy (TEM) to examine dried inks and electrode structures from different solvents; determined that all solvents used in study do not cause notable Pt displacement on carbon under our conditions, but solvent choice may have an effect on Pt particle growth during potential cycling.
- Initiated bilayer/gradient electrode work; demonstrated that Nafion[®] content changes response of electrode to humidity conditions.

Introduction

With improved electrode structures, less platinum catalyst could be used in polymer electrolyte fuel cells, reducing the cost and increasing the chances of widespread commercialization. Optimized electrode structures are also necessary to maximize durability and performance under varied conditions, such as with voltage, temperature, and humidity changes. As new catalyst materials and structures emerge, a better understanding of how to incorporate such materials into well-performing electrodes is also required.

Fuel cell electrodes are prepared by combining a dispersed, ionically-conducting polymer (ionomer) with carbon-supported Pt particles in a solvent medium. After further additions (solvents, ionic compounds, etc.), the mixture, called an ink, is painted or sprayed onto the desired surface and dried at elevated temperature.

These many steps have only been partially optimized empirically. At the end, the electrode structure must carry out three types of transport effectively: (1) electronic; (2) ionic; and (3) mass (gases and water). This is accomplished through interpenetrating networks of catalyst, ionomer, and pores, and the organization of the materials at many length scales may be important.

The purpose of this study is to examine the details of the Pt-ionomer interface, how the electrode structure evolves, and to determine how processing conditions affect the final electrode structure. Using a variety of characterization techniques that span multiple length scales, we seek to provide a more complete picture of the formation and function of electrode structure than is currently available.

Approach

The analytical capabilities of LANL have been leveraged to examine the formation of electrode structure across many length scales, including neutron scattering methods, NMR, atomic force microscopy (AFM), and TEM. These techniques allow for the correlation of data from the inks used to prepare fuel cell electrodes to the observed final electrode structure and performance. Ionomer mobility (NMR), particle size and internal structure (neutron scattering), tendency to phase-segregate (AFM), and Pt-carbon size and spatial distributions (TEM) are examples of the information that we have collected in relation to our optimization efforts.

Results

As mentioned above, fuel cell electrodes are prepared using ionomer dispersions in solvent that are combined with the catalyst. In FY 2009, we focused on understanding how the solvent choice (1) affected the structural and chemical properties of the ionomer in the dispersed and dried states, and (2) how those properties related to the observed fuel cell performance of electrodes prepared from the different ionomer dispersions. To carry out this study, a method to prepare ionomer dispersions from Nafion® 212 in a variety of solvents was developed and submitted for a patent [1]. Some additional work using bilayer electrodes was also initiated, to address a larger length scale of electrode design.

As shown in Figure 1, the performance of membrane electrode assemblies (MEAs) with cathodes prepared from inks containing different solvents varied greatly. The MEA with a cathode prepared from n-methylpyrrolidone (NMP-cathode) performed better in the kinetically-controlled region of the plot, whereas the MEA with a cathode prepared from a glycerol ink (glycerol-cathode) performed better at mass-transport controlled current densities above 0.70 V. The propylene-glycol cathode gave an intermediate

FIGURE 1. Polarization curves of fuel cell MEAs prepared with cathodes cast from ionomer dispersions containing either n-methylpyrrolidone or glycerol solvent. Cell temp. 80°C; fully humidified; backpressure: 30/30 psig; Catalyst: 20% Pt/C (ETEK): 0.2/0.2 mgpt/cm², ionomer: Nafion® 212.

performance, but was more similar overall to glycerol. These observations raised questions about effect of solvent on the structure of the ionomer, as well as on the interactions of the catalyst and ionomer. A variety of techniques available to LANL staff were thus selected to begin to provide the required answers.

¹⁹Fluorine NMR was used to address the effect of solvent on the chemical environment of Nafion®. As shown in Figure 2, the mobilities of fluorines associated with the polymer backbone or, alternately, with the polymer sidechains are affected greatly the choice of solvent. The relative mobility of ionomer backbone and side-chain fluorines was calculated as indicated within the Figure 2 caption. In glycerol dispersion, the peaks corresponding to Nafion® backbone and sidechain fluorines are very broad, indicating decreased mobility. In contrast, in NMP or water solvent, the peaks corresponding to Nafion® fluorines are very sharp, demonstrating a higher mobility. The mobilities of the fluorines in propylene glycol were intermediate those in glycerol and NMP, but closer to glycerol, following a similar pattern to the fuel cell data.

Our working hypothesis developed from these observations is that the mobility of the polymer backbone and sidechains affects their ability to separate into phases, and that these differences may affect the final electrode structure. Indeed, our recent AFM studies of thick Nafion® films cast from glycerol-based and water-based dispersions show very different degrees of phase-separation of the hydrophobic and hydrophilic portions of the Nafion® chain [2]. Glycerol-cast films

FIGURE 2. (a) Depiction of Nafion® chemical structure with each type of fluorine labeled a-g; (b) assignment of NMR peaks using these labels; (c) plot of the relative mobilities of side-chain fluorines and backbone fluorines. Calculation of relative main-chain mobility: peak area (a) / peak area (c,e,f). Calculation of side chain mobility: 1 / line width of (c,e,f) peak (kHz⁻¹).

showed very little phase separation, whereas the water-cast film showed a high degree of phase separation. Thus, the lowered fuel cell performance may be due to the specific arrangement of side-chains containing sulfonic acids groups near the platinum catalyst particles. Of course, the behavior of thick Nafion® films cannot be directly related to fuel cell electrodes, and we continue to design experiments closer to the real case.

(a) Nafion® dispersion in NMP

(b) Nafion® dispersion in glycerol

FIGURE 3. Models of the structure of Nafion® dispersed in (a) NMP or (b) glycerol solvent as derived from neutron scattering data. Please see ref [2] for further details.

Neutron scattering experiments further support that the ionomer structure differs greatly depending on the solvent. The models of the Nafion® structure in glycerol and NMP as derived from small-angle neutron scattering data are shown in Figure 3. The data for Nafion® in glycerol can be fit well with a cylindrical model (less phase-separation) with little solvent penetration, whereas the NMP dispersion data require a core-shell model (more phase-separation) and solvent penetration to fit the data properly. These depictions are consistent with the lack of mobility observed by NMR and lack of phase-separation observed by AFM for Nafion® dispersed in glycerol, and vice versa for NMP dispersions. It is plausible, though not yet proved, that the final structures of the Pt-ionomer interfaces formed from such dispersions may also differ.

We have begun to examine water-isopropanol mixtures as solvents for ionomer dispersions, and the correspondences between the NMR mobilities and the fuel cell performances were consistent with those discussed above with respect to performance in the kinetically-controlled voltage range. The performance in the mass-transport controlled range was similar to glycerol-derived cathodes, however. This may reflect the importance of larger length scales than shown by NMR. Ongoing neutron scattering experiments and TEM imaging will show the structure at larger scales. Please see ref [2] for further details.

Besides the performance, the durability of cathodes cast from Nafion® dispersed in glycerol (glycerol cathode) and, water-propanol-isopropanol (W-P cathode) were compared, as shown in Figure 4. The performance of the W-P cathode was initially much

FIGURE 4. H_2 /air polarization curves of MEAs prepared from (a) W-P cathode and (b) Glycerol cathode before (initial) and after potential cycling (3k–30k cyclic voltammetry cycles). H_2/N_2 potential cycling condition [3]: 0.6–1.0 V, 50 mV/sec, 80°C, fully humidified. H_2 /air fuel cell test condition: 80°C, fully humidified, anode/cathode pressure = 30 psig; H_2 : 160 sccm; air: 550 sccm.

higher, but the cathode was affected more seriously by potential cycling. After 30k cycles, the glycerol cathode performed significantly better than the W-P cathode, suggesting a more durable electrode structure. The durability seems to be related in part to less Pt particle growth in the glycerol cathode with potential cycling, as shown by TEM [2]. This difference can result from the tendency of Nafion® to phase-separate more in water-propanol dispersions than in glycerol dispersions, as suggested by NMR and AFM studies. Verification of the increased tendency of Nafion® to phase separate in W-P solvent even after the addition of Pt/C is required, and this lack of information will be addressed with neutron scattering experiments of catalyst inks.

Initial studies involving bi-layer electrodes with different Nafion® content near the membrane versus the gas diffusion layer were also conducted. The electrodes responded differently to relative humidity, but no major performance enhancements were observed in these initial experiments.

Conclusions and Future Directions

We have begun a series of experiments that promises to follow the evolution of electrode structure in detail at multiple length scales. Already, correlations have been identified between the local mobility and structure of Nafion® dispersed in various solvents as determined by NMR and neutron scattering, and the performance and durability of fuel cell cathodes prepared from those dispersions. Solvents that increase Nafion® mobility and phase-separation enhance the performance in the kinetically-controlled voltage region, whereas pure solvents that hinder the mobility tend to show better performance in the mass-transport controlled voltage range. The solvent also has a marked effect on durability of the generated electrodes to potential cycling.

Overall, we intend to continue to move our experiments towards more accurately reflecting the true conditions used to form electrode structures. Specifically, we plan to (1) further explore solvent mixtures rather than pure solvents, (2) add Pt/carbon to the measurements, and (3) more thoroughly characterize the MEAs with alternating current impedance, oxygen experiments, etc.

Special Recognitions & Awards/Patents Issued

1. Y.S. Kim, T. Rockward and K.-S. Lee, US Patent Application (2009).

FY 2009 Publications/Presentations

- 214th Meeting of the Electrochemical Society, Honolulu, HI, October 12–17, 2008. Title: “Measurement and Understanding of Catalyst Utilization in Fuel Cells.” C.M. Johnston, H. Xu, E.L. Brosha, J. Chlistunoff, K. More, E. Orlor, M. Hawley, and B. Pivovar.
- Canada to USA Fuel Cell and Hydrogen Cluster Connection Workshop, Vancouver, BC, Canada, February 16–17, 2009. Title: “Studies Towards Optimizing Fuel Cell Electrode Structure and Composition.” E. Brosha, F. Garzon, C. Johnston, A. Labourieau, Y.S. Kim, K.-S. Lee, B. Orlor, B. Pivovar, D. Torracco, C. Welch, H. Xu.
- “The Effect of Ink Processing and Composition on Pt Utilization in Polymer Electrolyte Fuel Cells”, H. Xu, E. Brosha, K. More, F. Uribe, F. Garzon, B. Pivovar, J. Power Sources, in preparation.

References

- Y.S. Kim, T. Rockward and K.-S. Lee, US Patent Application (2009).
- C.M. Johnston, Applied Science for Electrode Cost, Performance, and Durability, in *DOE Hydrogen Program Annual Merit Review and Peer Evaluation* (2009).
- U.S. DOE Cell Component Accelerated Stress Test Protocols for PEM Fuel Cells (2008).

V.A.7 Microstructural Characterization of PEM Fuel Cell MEAs

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Project End Date: Project continuation and direction determined annually by DOE

Objectives

- Develop new, innovative microanalysis and imaging techniques to characterize polymer electrolyte membrane fuel cell (PEMFC) material constituents before, during, and after electrochemical aging.
- Elucidate membrane electrode assembly (MEA) degradation and/or failure mechanisms by conducting extensive microstructural characterization using advanced electron microscopy techniques (comparing as-processed and electrochemically-aged MEAs).
- Develop correlations between MEA structure/composition and durability/performance.
- Collaborate with PEMFC component developers and manufacturers, university researchers, and other national laboratories, to evaluate MEAs using electron microscopy and complimentary microstructural/compositional analysis techniques; provide feedback for MEA optimization.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells, and Infrastructure Technologies (HFCIT) Program Multi-Year Research, Development and Demonstration Plan:

- (A) Durability
- (B) Cost
- (C) Performance

Technical Targets

This project is focused on conducting fundamental characterization studies on the stability of individual constituents comprising PEMFC MEAs. Of primary importance is relating MEA microstructural changes during aging to fuel cell durability and performance. Long-term MEA aging studies are being conducted in collaboration with numerous external partners, including MEA manufacturers, PEMFC stack manufacturers, universities, and national laboratories. ORNL research is focused not only on the pre- and post-mortem analysis of powders, membranes, and MEAs, but also on the development and application of in situ microscopy techniques to elucidate degradation mechanisms that contribute to limiting the life of PEMFCs. Insights gained will be applied toward the design and manufacture of MEAs that meet the following DOE 2010 MEA targets:

- Cost: $\leq \$15/\text{kW}$
- Durability with cycling: $\leq 80^\circ\text{C}$ – 5,000 h;
 $> 80^\circ\text{C}$ – 2,000 h
- Operating temperatures: $\leq 120^\circ\text{C}$
- Total catalyst loading (for both electrodes):
0.33 g/kW (rated)
- Extent of performance degradation over lifetime:
10%

Accomplishments

- Acquired and evaluated a Si-drift detector (SDD) for energy dispersive spectroscopy (EDS) on the JEOL 2200 aberration-corrected scanning transmission electron microscopy (STEM) for Å-scale compositional analysis and elemental mapping – this new technology results in a 5-10 fold increase in the spatial resolution for EDS.
- Acquired and conducted initial ‘proof-of-principle’ testing of a new specialized liquid cell holder for in situ electrochemical testing of fuel cell materials in the Hitachi HF-3300 transmission and scanning transmission electron microscopy (TEM-STEM).
- Acquired and utilized a new 360° rotation-tomography holder to study catalyst distributions on different support materials.
- Developed ultra-low-angle microtomy (ULAM) technique to evaluate the through-thickness compositional/chemical nature of polymer membranes and electrodes within an MEA.
- Continued collaboration with Brookhaven National Laboratory (BNL) to characterize their Pt-ML alloy catalysts using high-angle annular dark field (HAADF)-STEM.

- Continued collaboration with 3M to characterize nano-structured thin film catalyst samples using HAADF-STEM.
- Supported a full-time graduate student from Rensselaer Polytechnic Institute working on microstructural characterization of phosphoric acid-doped polybenzimidazole membranes.
- Conducted extensive alloy catalyst nanoparticle characterization studies using sub-Å resolution HAADF-STEM, including in situ microscopy studies using a specialized heating holder to observe catalyst coalescence.

Introduction

PEMFCs are being developed for future use as efficient, zero-emission power sources. However, the performance of PEMFCs degrades rapidly with time at elevated temperature (currently limited to ~80°C) during electrochemical aging. Performance degradation can be attributed to the durability of individual components comprising the MEA, such as the electrocatalyst, catalyst support, and/or the proton-conducting polymer membrane. However, many of the mechanisms contributing to decreased stability within the MEA during long-term electrochemical aging are not fully understood. During the past several years, the Microstructural Characterization Program at ORNL has been focused on forming collaborative relationships with numerous industrial PEMFC developers/manufacturers, universities, and national laboratories, to utilize advanced microscopy techniques to evaluate as-fabricated and electrochemically-aged PEMFC MEAs and to characterize individual PEMFC material components. These studies are used to establish critical processing-microstructure-performance relationships and to elucidate MEA degradation and failure mechanisms. Understanding the structural and compositional changes to the materials comprising the MEA during electrochemical-aging will allow for the implementation of processing changes and critical materials development that are required for optimized PEMFC durability and performance.

Approach

The microstructural characterization task utilizes advanced electron microscopy techniques to characterize the individual material components comprising PEMFCs, before and after incorporation into an MEA. Traditionally, fuel cell degradation has been studied by evaluating MEAs before and after electrochemical testing. While a significant portion of the ORNL research still focuses on characterizing fuel cell materials this way (established collaborations with

Los Alamos National Laboratory, for instance), there has been a recent shift in the ORNL research to focus on the development and implementation of in situ microscopy techniques, i.e., using a specialized liquid cell holder, to study fuel cell materials degradation at high spatial and temporal resolution. Proof-testing of a recently designed liquid holder has been conducted using a fuel cell catalyst.

The HAADF-STEM technique, commonly referred to as Z-contrast imaging, allows for Å-scale imaging of the atomic structure of a catalyst particles based on atomic number (Z) differences, has been used to characterize many different alloy catalyst compositions, and has recently been complimented by the addition of an SDD for the simultaneous acquisition of compositional data (line scans, elemental maps, etc.) from nanoparticles. The combination of in situ microscopy and the ability to image and analyze materials at the sub-nm scale using an aberration-corrected electron microscope, will enable the direct interpretation of the critical phenomena contributing to fuel cell degradation during electrochemical aging.

The research effort in FY 2009 was focused on the initial stages of development, optimization, and application of three primary characterization techniques for the evaluation of fuel cell materials; (1) imaging surfaces and core-shell morphologies of alloy catalyst systems using HAADF-STEM coupled with compositional analysis of the nanoparticle using the new SDD on the aberration-corrected STEM, (2) the development of an in situ electrochemical cell for high spatial and temporal resolution in an electron microscope, and (3) development of a new technique for sectioning MEAs for analysis by X-ray photoelectron spectroscopy (XPS). Significant progress has been made in each of these focus areas.

Results

In Situ Microscopy of Fuel Cell Materials

During FY 2009, initial testing of the liquid flow cell holder (made for the Hitachi HF3300 TEM/STEM) was conducted. For these initial assessments, the liquid cell was filled with a dilute saline solution + 20% Pt₃Cr on Vulcan fuel cell catalyst. These ‘proof-of-principle’ tests were designed to evaluate two primary features of the liquid cell: (1) the thickness of the liquid gap as well as the ability of the cell to hold a flowing and a non-flowing liquid and (2) the image resolution in STEM mode.

A picture of the specimen holder and a schematic of the flow cell are shown in Figures 1(a) and 1(b), respectively. The holder design is based on an initial liquid cell design by de Jonge, et al. [1]. The cell is composed of two small (2 mm by 3 mm) Si chips with a thin layer of (electron-transparent) silicon nitride

(~50 nm) on the opposing surfaces. A small region on the back side of the Si chips is etched away to the silicon nitride layer, forming an electron transparent “window” for transmission of the electron beam and imaging of the solid material(s) held within the liquid-filled gap.

A 20% Pt₃Cr supported on Vulcan carbon black (Pt/C) was dispersed in a dilute saline solution (provides a conductive liquid). A 2 mL droplet was applied to the “top” silicon nitride surface (across window) and the “bottom” chip was placed on the surface. To create a somewhat reliable gap thickness and to protect the windows from any sharp edges of the solid material that could cause the windows to break, small latex spheres (~5 μm diameter) were applied to the edges of the silicon nitride surface of the top window. Once the liquid-filled cell was secured in place at the tip of the holder (see Figure 1(a)), the holder was inserted into the column of the Hitachi HF3300 TEM/STEM.

Figure 2 demonstrates the image quality (and resolution) for this initial test; Figure 2(a) shows an image of the Pt₃Cr/C not held within the cell (normal image in vacuum), Figure 2(b) shows an image of the Pt₃Cr/C imaged through the two silicon nitride windows (no liquid in the cell), and Figure 2(c) is an image of the Pt₃Cr/C imaged through a 7 mm thick liquid layer (the gap thickness measured for this test). The images are HAADF STEM images, where the Pt₃Cr particles image

“brightly” as a result of their high atomic number. In this initial test, a <3 nm resolution was demonstrated for the Pt₃Cr particles (Figure 2(c)).

FIGURE 1. (a) New liquid-cell holder (developed in collaboration with Hummingbird Scientific) for the Hitachi HF3300 TEM/STEM. Red circle designates “tip” where liquid cell is held. (b) Schematic of liquid cell used for evaluating catalysts immersed in a liquid layer.

FIGURE 2. (a) Conventional HAADF-STEM of Pt₃Cr/C (no liquid), (b) HAADF-STEM image of Pt₃Cr/C imaged through two silicon nitride windows (no liquid), and (c) Pt₃Cr/C imaged through a 7 μm thick saline solution layer demonstrating ~3 nm resolution.

High Spatial Resolution EDS of Nanoparticles

Research in FY 2009 has also focused on the evaluation of an EDS system recently installed on ORNL's aberration-corrected STEM, the JEOL 2200FS. The manufacturer of the EDS system being evaluated is Bruker and the major improved component of this system is the incorporation of an SDD. There are numerous advantages to SDD technology, including fast EDS spectrum imaging and data acquisition, as well as high geometric collection efficiency which can be extremely important for beam-sensitive materials. In addition modern SDDs are actually providing better spectral resolution (<125 eV) than traditional Si-Li detectors. The Peltier cooling completely eliminates the need for a large liquid nitrogen dewar hanging off the column, removing concerns about image degradation from either liquid nitrogen boiling or enhanced acoustic coupling with background noise in the instrument environment. Though SDDs are primarily available for SEMs, the technology is slowly becoming available for TEM/STEM instruments. Though the high count rate (e.g., <100 kcps) capability of an SDD is not the critical specification for most TEM/STEM instruments (especially aberration-corrected instruments), the large geometric collection efficiency and operation of SDDs will be very important. Thus, we are comparing this technology with data collected on our non-aberration-corrected STEM instruments using conventional Si-Li EDS detectors and its applicability to the compositional characterization of nanoparticles (catalysts).

The major limitation for characterizing small particles by EDS in a STEM is the probe diameter and the low count rate – since many catalyst particles are <3 nm in diameter, there are clear limitations regarding data collected from different areas of individual particles. Data acquired on very small particles has been limited to “bulk” or average particle compositions. It has been virtually impossible to identify core-shell, surface-enrichment, etc. from data for extremely small particles and reliable data interpretation must be limited to the larger particles in the distribution regarding elemental segregation. The advantage for adding EDS data acquisition capabilities to an aberration-corrected instrument is clearly the reduced probe size to <1 Å and increased beam current. The probe can be scanned across much smaller areas/particles to evaluate compositional segregation effects.

The improvement in the spatial resolution of data acquired using the SDD on the aberration-corrected STEM is increased by a factor of 5-10X and is illustrated by the line scan and elemental maps collected from Pt-ML/Pd/C catalysts produced by BNL shown in Figure 3(a) and 3(b), respectively. The ~ 1.5 nm Pt-enriched shell surrounding the Pd-core is clearly evident in both the map and the line scan in Figure 3, confirming the initial observations of a core-shell structure by HAADF-STEM imaging, as shown in Figure 3(c).

FIGURE 3. (a) Line scan and (b) elemental maps collected from Pt-ML/Pd/C catalysts produced by BNL. The ~ 1.5 nm Pt-enriched shell surrounding the Pd-core is clearly evident in both the map and the line scan confirming the initial observations of a core-shell structure by (c) the corresponding HAADF-STEM image.

ULAM of Fuel Cell MEAs and Polymer Membranes for XPS

In order to conduct chemical/compositional analyses of membranes and MEAs via XPS, i.e., cross-sectional XPS profiles through the “bulk” membrane, a novel technique for preparing angle-cut microtome

sections has been developed at ORNL. XPS analyses of polymer membranes can be quite challenging for several reasons; (1) the typical thickness of polymer membranes is 10-20 μm and the minimum X-ray spot-size for XPS is $\sim 30 \mu\text{m}$, thus analyses have been limited to the air and film (substrate) surfaces only, which do not provide information regarding the bulk (or through-thickness) composition of the membranes and if an electrode is on the surface (as for an MEA), the membrane surfaces can not be analyzed, (2) depth-profiling from the surface into the membrane by sputtering is not a viable option since the membranes are easily damaged by the sputtered ions, and (3) the polymer membranes are easily damaged by the X-ray beam and data must be accumulated relatively rapidly (within several minutes). To this end, polymer membranes and MEAs are being prepared by significantly elongating the cross-sections using ULAM. The membranes are positioned in an epoxy block such that the diamond knife sections through the membrane at a fairly shallow angle, creating an elongated section through the thickness. This is illustrated in Figure 4 – MEA and membrane cross-sections having widths of 100-400 μm have been prepared using this technique.

FIGURE 4. Image comparing ULAM-prepared MEA and conventional MEA - MEA and membrane cross-sections having widths of 100-400 μm have been prepared using the ULAM technique.

Conclusions and Future Directions

Conclusions

- Several new collaborations have been established during the past year that have accessed the unique imaging (microscopy) capabilities at ORNL via:
 - Work-for-Others (proprietary research).
 - Shared Research Equipment (SHaRE) User Program (non-proprietary research) - University of Houston, University of Texas, University of Connecticut, Rensselaer Polytechnic Institute.
 - Baseline HFCIT-sponsored PEM-MEA Characterization Program (non-proprietary).
- Progress to date to develop in situ liquid STEM as a viable technique to monitor the degradation of PEMFC materials has been slower than expected in FY 2009 – several critical issues have yet to be resolved, but initial ‘proof-of-principle’ tests have been conducted to demonstrate a $<3 \text{ nm}$ resolution in a 7-9 μm thick layer of water.
- The addition of SDD technology to the aberration-corrected high spatial resolution STEM will enable $<2 \text{ \AA}$ compositional analysis – optimization of data collection parameters will be ongoing.
- ULAM has been established as a unique and reproducible technique to prepare membranes and MEAs for cross-sectional XPS analysis.

Future Directions

- Continue to evaluate and add capabilities to the in situ liquid microscopy holder for high spatial and temporal resolution microscopy of PEMFC material constituents operated under relevant operating conditions – liquid electrolytes, temperature, potential cycling, etc. This will be a significant research effort in FY 2010.
- Further develop 3-dimensional tomography methods for characterizing fuel cell materials (catalyst particle coalescence, carbon support degradation, etc.).
- Continue to establish new collaborations with industries, universities, and national laboratories (including access via ORNL User Facilities) to facilitate “transfer” of unique capabilities.
- Support new DOE projects with microstructural characterization and advanced characterization techniques.

Special Recognitions & Awards/Patents Issued

1. Research selected as one of the top three FreedomCAR Fuel Cell Tech Team – DOE Highlights/Accomplishments for 2008.

FY 2009 Publications/Presentations

1. K.L. More, L.F. Allard, and K.S. Reeves, "Atomic-Scale Characterization of the Stability of PEM Fuel Cell Cathodes," invited presentation at the Gordon Research Conference on Aqueous Corrosion, July 21, 2008.
2. K.L. More, L.F. Allard, and K.S. Reeves, "In-situ Microscopy Characterization of Catalyst Degradation," invited presentation at CARISMA-Progress MEA, September 24, 2008.
3. K.L. More, L.F. Allard, and K.S. Reeves, "Atomic-Scale Imaging of Pt-Based Catalyst Particle Coalescence During Low-Temperature In-situ Heating," presentation at 214th Meeting of The Electrochemical Society, October 14, 2008.
4. K.L. More, L.F. Allard, and K.S. Reeves, "Atomic-Scale Characterization of Catalyst Particles for PEM Fuel Cell Cathodes," invited presentation at TMS 2009 – 138th Annual Meeting, February 18, 2009.
5. P. Strasser, S. Koh, T. Anniye, J. Greeley, K.L. More, S. Kaya, H. Ogasawara, M.F. Toney, and A. Nilsson, "Lattice-Strain Controls Unique Catalytic Activity in Dealloyed Core-Shell Pt Bimetallic Nanoparticles," submitted to *Nature Materials*.
6. G. Gupta, D. Slanac, P. Kumar, J. Wiggins, X. Wang, S. Swimmer, K.L. More, S. Dai, K. Stevenson, and K. Johnston, "Highly Active and Exceptionally Stable Pt-Cu Oxygen Reduction Electrocatalysts Supported on Mesoporous Graphitic Carbon," submitted to *Journal of The American Chemical Society*.

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V.A.8 Neutron Imaging Study of the Water Transport in Operating Fuel Cells

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Objectives

- Provide neutron imaging-based research and testing infrastructure to enable the fuel cell industry to design, test, and optimize prototype to commercial grade fuel cells.
- Provide secure facility for proprietary research by industry. Make open research data available for beneficial use by the general fuel cell community.
- Continually improve and develop methods and technology to accommodate rapidly changing industry/academia needs.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section (3.4.4.2) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) Durability
- (D) Air, Thermal and Water Management

Accomplishments

- Quantification of measurement uncertainties in the water volume of fuel cells using neutron radiography due to systematic effects:
 - The contributions to measurement error from possible systematic effects have been measured or estimated and none explain the discrepancies between the modeling and the measured through-plane water content.
 - Measurement of Nafion® water uptake as a function of water activity with high resolution neutron radiography is consistent with existing,

published, gravimetric measurements, giving further support that the neutron radiography systematic uncertainties are sufficiently understood.

- High resolution neutron imaging of fuel cells:
 - Visualization of water transport due to thermal gradients reveals the importance of boundary conditions in phase change induced flow.
 - Factor of five improvement in geometrical spatial resolution with new slit apertures without sacrificing overall intensity (optimized for fuel cell imaging).
 - New high spatial resolution system with higher event rate has been tested for operation and is undergoing deployment.
 - Additional backup high resolution detector systems coming online to ensure reliable operation of the imaging facility for fuel cell users of the facility.
- Improvements to the facility impacting fuel cell radiography:
 - New apertures discussed previously allows dramatic improvement of resolution of anode vs. cathode.
 - New EIS-Zahner IM6eX electrochemical workstation for fuel cell impedance spectroscopy measurements.
 - New imaging acquisition software developed by NIST and tailored to the fuel cell facility users.

Introduction

At NIST, we maintain the premier fuel cell neutron imaging facility in the world and continually seek to improve its capabilities. This facility provides researchers a powerful and effective tool to visualize and quantify water transport inside operating fuel cells. Imaging the water dynamics of a PEMFC is carried out in real time with the required spatial resolution needed for fuel cells that are being developed today. From these images, with freely available NIST-developed image analysis routines, PEMFC industry personnel and researchers can obtain in situ, non-destructive quantitative measurements of the water content of an operating PEMFC. Neutron imaging is the only in situ method for visualizing the water distribution in a “real world” PEMFC. Unlike X-rays, whose interaction with materials increases with the number density of electrons, neutrons interact via the nuclear force, which varies somewhat randomly across the periodic table,

and is isotopically sensitive. For instance, a neutron's interaction with hydrogen is approximately 100 times greater than that with aluminum, and 10 times greater than that with deuterium. It is this sensitivity to hydrogen (and insensitivity to many other materials) that is exploited in neutron imaging studies of water transport in operating fuel cells.

Approach

The typical scales of interest in a PEMFC are: channels approximately 1 mm wide and 1 mm deep, the gas diffusion media is 0.1 mm to 0.3 mm thick, the membrane is 0.01 mm to 0.05 mm thick, and the active area is 50 cm² to 500 cm². Thus, to study in situ, nondestructive water/hydrogen transport in PEMFCs while in operation and hydrogen transport/distribution in hydrogen storage media we will develop new facilities and improve existing capability for obtaining high spatial and temporal resolution neutron imaging. Employing the mathematical models of neutron scattering, we will develop a software suite that enables users to obtain quantitative measurements of the water content in an operating PEMFC. Due to the complexity of PEMFCs and the large number of open questions regarding water transport in PEMFCs, we will develop partnerships with industry and academia to train them in the use of the facility, collaborate with them on research projects, and seek their feedback to pursue future technical breakthroughs.

Results

This year the staff of the NIST Neutron Imaging Facility have focused on developing a detailed understanding of systematic errors that can affect the quantification of water in neutron radiography experiments on fuel cells. We have assessed a large set of potential measurement uncertainties in the membrane water content including, non-Lambert-Beer law behavior due to beam hardening, changes in the background, spatial resolution, and differences in the scattering properties of water absorbed in Nafion[®]. This work was required to address a large discrepancy observed in the published literature between current estimates of the membrane water content during fuel cell operation and that measured by neutron radiography. We have worked in collaboration with the Los Alamos National Laboratory fuel cell team and the modeling effort at Lawrence Berkeley National Laboratory on this project. We performed calibration measurements with a stepped wedge of water with thicknesses the same as those encountered in measurements of liquid saturated membranes. The uncertainty in the results was dominated by the expected uncertainty due to the beam intensity (Poisson counting noise). This showed that there was no systematic deviation from the exponential law of attenuation (Lambert-Beer law). One source

of deviation is expected due to beam hardening, but the thickness of water that is typically encountered in PEMFCs used in high resolution imaging experiments is insufficient to cause a deviation from the exponential law calibration technique. Another source of deviation is expected due to incorrect accounting of the scattered neutron background, due to the fuel cell or water, an effect that changes with water thickness. This scattering contribution is small, and does not cause a statistically measurable deviation from the exponential law behavior. A third source of deviation can come from incorrectly subtracting the gamma-ray background. However, the systematic uncertainty introduced by incorrectly accounting for the gamma-ray background as well as the scattered neutron background is at least an order of magnitude smaller than the counting statistics uncertainty typical of high resolution PEMFC images. We have identified a large systematic error due to the finite spatial resolution of the imaging detector. This resolution effect can result in the measured water content being systematically suppressed in small regions. An example where this is most important is the high resolution measurement of water in the through-plane direction. Here the membrane is a thin water saturated region. The rapid change in water content between anode, membrane and cathode can be suppressed due to the finite spatial resolution of the neutron imaging detector. There are mathematical models (deconvolution) that allow one to sharpen an image in order to reduce this effect. However this typically introduces additional noise to the measurement (there may be algorithms that are more appropriate for the high variability of the high resolution neutron image data). A more robust approach is to simulate neutron images from a model prediction of the through-plane water content. The effect of the resolution of the imaging system can be modeled as a convolution of a Gaussian with the predicted water content. This enables direct comparison of model prediction with the neutron data in order to test the sensitivity of the measurement system towards discriminating between different water profile predictions. Another way to avoid this resolution issue is to make the membrane thicker. With a thicker membrane the uncertainty is reduced and/or nearly eliminated. Doing this is critical to decouple any uncertainties arising from a change in the neutron scattering cross section for water absorbed in Nafion[®]. To do this, special 1 mm thick Nafion[®] membranes were prepared (Ion Power, Inc.) to measure the water sorption in Nafion[®] with neutrons. A deviation from published gravimetric measurements could indicate that water in Nafion[®] has different scattering properties than free water. In this case, the water distribution was observed to be uniform over a large region in the center of the membrane, indicating that the finite resolution is not affecting the measurement. We measured the membrane water content as a function of water activity (relative humidity = 50%, 75%, 90%, liquid saturated,

etc.) and as shown in Figure 1 have found that the neutron radiography results agree within the estimated uncertainties with the values reported from gravimetric methods. Therefore, the neutron cross-section of water in Nafion® is the same as free water. Since the finite resolution effect can result in a severe reduction of the observed membrane electrode assembly water content we have modified the neutron imaging facility to minimize this effect and optimize it for fuel cell use. To improve the spatial resolution due to the geometric blur of the neutron beam, we have introduced a vertical and horizontal slit that reduces the geometric blurring by a factor of 5 along the through-plane direction. By using a slit instead of an aperture the intensity (and therefore the required exposure time) can be maintained avoiding a decrease in the dynamic resolution of the beam. Improvements in the detector spatial resolution are also expected to minimize this effect. These results have been submitted to a peer-reviewed journal, and publication is expected within a year.

Researchers from the Pennsylvania State University used the NIST BT2 high resolution neutron imaging facility to visualize the liquid water flow in the through-plane direction under different thermal gradients (Figure 2). In these tests, two sets of GDLs were studied, one with only a substrate loading of polytetrafluoroethylene (PTFE) of 5% by weight and a microporous layer, and with no PTFE content. Initially, one side of the fuel cell assembly was filled with liquid water, while the other side had only vapor, and the two sides were maintained at different temperatures. The GDL with no PTFE showed a slight water flow with no thermal gradient due to a small piezometric head.

FIGURE 1. Measured membrane water content with high resolution neutron radiography as a function of water activity compared with correlations derived from gravimetric studies. The neutron radiography measurement agrees within uncertainty with the established ex situ data.

Applying a thermal gradient, so that the liquid side was cooler, prevented this slow leakage water flow. Reversing the thermal gradient resulted in significantly higher fluid flow than in the case of that driven by the piezometric head. Images of the GDL containing PTFE showed that with no thermal gradient or when the liquid side was maintained at a colder temperature, the piezometric head was insufficient to induce flow through the hydrophobic diffusion media. However, when the gas-phase side of the test section was colder, the channels were observed to fill rapidly (few minutes) due to phase change induced flow. This visualization work elucidated the critical importance of the vapor boundary layer to phase change induced flow, and was in support of an extensive set of ex situ measurements of thermo-osmosis and phase change induced flow rates in typical fuel cell porous media (Kim, 2009).

As part of the NCNR expansion initiative, we are building a cold neutron imaging facility. This is motivated by the fact that the cross section of water increases as the neutron velocity decreases. As a result cold neutrons have a larger scattering cross-section from water and the detection efficiency in the neutron imaging detector is about a factor of 2 higher. For equal intensity neutron beams, this means that a cold imaging facility will have about a factor of 4 improvement in the water measurement uncertainty. This was confirmed by measuring the attenuation coefficient at a temporary location imaging at the NCNR, and Figure 3 demonstrates that the attenuation coefficient is a factor of two larger for cold neutrons than for thermal neutrons. A set of PEMFC experiments were conducted in collaboration with General Motors, and this data is still under analysis.

In addition, we continue to develop our fuel cell and hydrogen infrastructure. We have added a Zahner electrochemical workstation for in situ electrical impedance spectroscopy and neutron imaging experiments and future segmented or multi-cell experiments. We are in the process of developing a

FIGURE 2. Visualization of phase change induced flow with hydrophobic gas diffusion media performed with high resolution neutron radiography.

FIGURE 3. Comparison of the Attenuation Coefficient of Water for Thermal and Cold Neutrons

hydrogen distribution manifold for studying hydrogen storage materials. We also plan to add independent anode and cathode temperature control to the fuel cell test stand to enable the measurement water transport phenomena due to thermal gradients.

Conclusions

We have investigated potential sources of systematic measurement uncertainty to ensure data integrity and found that the sources of error cannot fully explain discrepancies between observed and predicted water thicknesses. We have written new analysis code for users to simulate high resolution neutron images to better compare measurement with model predictions. We are collaborating with Los Alamos National Laboratory and Lawrence Berkeley Laboratory to design experiments and improved image analysis to understand the observed discrepancy. We continue to improve and develop our facility for improved image and measurement quality and test and control capabilities.

Future Directions

- Measurement of electroosmotic drag in membranes and gas diffusion coefficients in gas diffusion layers which incorporates improved uncertainty analysis. This work will be aided by development of image simulation from input models. The uncertainty analysis will be transferred to facility users as part of the standard image analysis suite.
- Continue advancement of imaging technology and capabilities at the facility, including deployment of a high resolution (better than 15 μm) imaging detector for general user base, design of a cold neutron imaging facility, and implementation of independent

anode/cathode temperature control into test stand for routine use.

FY 2009 Publications/Presentations

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Presentations and Conference Proceedings

1. D.S. Hussey and D.L. Jacobson, "Systematic Uncertainties in Neutron Imaging of Proton Exchange Membrane Fuel Cells", *Meet. Abstr. - Electrochem. Soc.* 802 939 (2008).
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V.B.1 Water Transport Exploratory Studies

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Start Date: March 2007
Project End Date: 2011

Objectives

- Develop understanding of water transport in polymer electrolyte membrane (PEM) fuel cells:
 - Non-design-specific (as possible).
- Evaluate structural and surface properties of materials affecting water transport and performance.
- Develop (enable) new components and operating methods.
- Accurately model water transport within the fuel cell.
- Develop a better understanding of the effects of freeze/thaw cycles and sub-freezing operation.
- Present and publish results.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program

Multi-Year Research, Development and Demonstration Plan:

(D) Water Transport within the Stack

Technical Targets

- Energy efficiency (65% at 25% rated power, 55% at 100% rated power)
- Power density (2,000 Watt/L)
- Specific power (2,000 Watt/kg)
- Cost (\$25/kWe)
- Start-up time to 50% power (30 seconds from -20°C, 5 seconds from 20°C)
- Freeze start operation (unassisted start from -40°C)
- Durability with cycling: 5,000 hrs

Accomplishments

Direct water imaging by neutron radiography and X-ray tomography

- Measured equilibrium water content in the membrane.
 - Lower water concentrations typically measured for operating membrane electrode assemblies (MEAs) with catalyst layers and gas diffusion layers (GDLs) compared with equilibrium values.
- Imaged water with variation of operating parameters.
- Imaging of water response to transients.
 - Evaluated fast membrane wetting compared with slow GDL de-wetting.

Segmented cell operation

- Measured water variation as a function of GDLs, inlet relative humidity (RH), cell position.

Freeze/thaw examination of PEM fuel cells

- Imaging of water/ice in fuel cells operated at sub-freezing temperatures.
- Monitoring where water freezes as a function of operating variables testing.

Evaluation and characterization of GDLs

- Profiling the GDL in 3-dimensions.
 - Observed water location in the GDL pore structure.

- Correlated water with Teflon[®] content in the GDL.

Varied micro porous layer (MPL) and substrate Teflon[®] loadings and cell operating conditions

- Neutron imaging and electrochemical impedance spectroscopy (EIS) were used to measure water content and performance.

Modeling of mass transport losses

- Using characterization data to develop comprehensive GDL water transport model in addition to the existing membrane/electrode model.

Introduction

Effective control of water distribution can be a major impediment to implementation of polymer electrolyte membrane fuel cells. Several important cell parameters, including membrane conductivity and mass transfer resistance within porous electrodes, are intimately linked to water distribution, requiring effective management of water in order to maximize fuel cell performance. Components such as the membrane and electrode layers require sufficient water to be present in order to allow adequate proton conductivity. Conversely, excess water within the system leads to mass transfer losses and can require additional balance-of-plant costs (extra energy or weight for increased humidification). The range of conditions under which the system is required to operate makes meeting all these requirements at the same time even more difficult. The conditional extremes provide the biggest challenges: maintaining hydration under hot/dry conditions and preventing flooding/dealing with ice formation under cold/wet conditions. Perhaps the most challenging of these conditions is subfreezing temperatures. In order to compete with internal combustion engines, the U.S. Department of Energy has stated goals for fuel cell survivability (-40°C), start-up time (30 seconds to 50% rated power from -20°C), and energy (5 MJ) under subfreezing conditions. In order to address these challenges there is a need for increased understanding of water transport and phase change within fuel cell components. This requires that the structure and properties of fuel cell materials be fully understood. The materials ultimately employed will need durability under normal and transient operations while allowing effective water management under any environmentally-relevant condition.

To achieve a deeper understanding of water transport and performance issues associated with water management, a multi-institutional and multi-disciplinary

team with significant experience investigating these phenomena has been assembled. This team is headed by Los Alamos National Laboratory (LANL) and includes Sandia National Laboratories, Oak Ridge National Laboratory, a university (Case Western Reserve University), an MEA supplier (W.L. Gore), a GDL supplier (SGL Carbon Group), and the National Institute of Standards and Technology. This report describes our Fiscal Year 2009 technical progress related to understanding the complex phenomena related to water transport within operating PEM fuel cells.

Approach

Our approach to understanding water transport within fuel cells is structured in three areas: fuel cell studies, characterization of component water transport properties, and modeling of water transport. These areas have aspects that can be considered free-standing, but each benefit greatly from work performed in the other areas. The modeling studies tie together what is learned during component characterization and allow better interpretation of the fuel cell studies. This approach and our team give us the greatest chance to increase the understanding of water transport in fuel cells and to develop and employ materials that will overcome water-related limitations in fuel cell systems.

To help understand the effect of components and operational conditions, we examine water transport in operating fuel cells, measure the water content and location of water during operation. In situ characterization of water content includes evaluation of the high frequency resistance (HFR) and by EIS to quantify the various limiting transport regimes and neutron imaging to visually measure the water content in the individual cell components at various locations. Variation of PEM components helps identify component effects on water management, with characterization of these components providing quantifiable water transport properties.

Results: Equilibrium Water Measurements in Nafion[®] by Neutron Imaging

Water transport in the ionomeric membrane, typically Nafion[®], has profound influence on the performance of the polymer electrolyte fuel cell, in terms of internal resistance and overall water balance. Prior neutron imaging and modeling based off of literature results show large discrepancy; up to a factor of 4 difference in membrane water content [1]. In FY 2009, we conducted high resolution neutron imaging of Nafion[®] membranes in order to measure water content and through-plane gradients in situ under disparate temperature and humidification conditions.

Several different experimental configurations were used, including 18 micron-thick membranes, N117 (~178 microns), a 3-layer sandwich of N117 (533 microns) and specially cast Nafion® membranes of 500 and 1,000 microns in thickness. 1,000-micron bare membrane exhibited significant swelling and blocked the parallel channels on both sides in a liquid-equilibration mode experiment. The same membrane in the MEA configuration was however sufficiently constrained by the adjoining catalyst layers and GDLs to avoid extensive swelling. High resolution neutron imaging was conducted with the membrane in the MEA configuration in both fuel cell and hydrogen pump modes. Representative water thickness response from neutron scattering data with the membrane in the MEA configuration is shown in Figure 1. The water distribution at the open circuit voltage (OCV) with 175% RH and 80°C temperature shows a distinctive plateau and the average water content, λ , was approximately estimated as 18.7. Furthermore, the water gradient response from such hydrogen pump mode experiments will be used to extract the electro-osmotic drag response of the membrane and correlated to fuel cell water balance. During hydrogen pump operation, the water gradient reverses when the potential is reversed, as expected. For this sample, there appears to be catalyst layer flooding on the anode side of the membrane, as evidenced by the peak at pixel 78.

Figure 2 shows the water profile for a 500 micron Nafion® membrane at OCV, 0.1 and 0.2 A/cm² fuel cell operation. These measurements were made at 40°C and 50% inlet RH. The membrane equilibrium water content at OCV was $\lambda = 5$, which agrees well with literature [2,3]. As the cell is operated under fuel cell mode, water is produced at the cathode catalyst, thus the water

FIGURE 1. Water distribution for a 1,000-micron cast Nafion® membrane in the MEA configuration at OCV, hydrogen pump and operating fuel cell modes. (80°C 175% RH)

FIGURE 2. Water distribution for a 500-micron cast Nafion® membrane in the MEA configuration at OCV, and operating fuel cell modes. (50/50% RH, 40°C)

content in the membrane increases in concentration to $\lambda = 7.1$ and $\lambda = 8.8$ for 0.1 and 0.2 A/cm² current densities. However, the membrane water content is much lower than often predicted during operation, as it is often assumed that the membrane will equilibrate with the liquid water produced at the cathode catalyst layer.

Results: Water Content Responses to Transient Operation

Fuel cells used in automotive drive cycles experience numerous and varied power transients. The water dynamics in the MEA during these transients can greatly affect performance and perhaps long-term durability. To examine the hydration of the PEM and GDL response to current step-up and step-down transients, water was measured in situ via neutron imaging with simultaneous HFR measurements. Figures 3a and 3b show HFR and water concentrations in the land region and channel regions in response to step transients in current.

Current step transients from 0.5 to 34.0 amps show MEA wetting occurs quickly, within 5 to 20 sec, while MEA drying, during the current transient from 34.0 to 0.5 amps, takes on the order of minutes (see Figure 3). This suggests that the primary wetting effect with increasing current is a fast process of membrane water absorption. The drying effect appears to be a slower diffusion process of water removal from the MEA/GDL.

Higher polytetrafluoroethylene (PTFE) loading in the more open porous structure of the GDL substrates allows for more rapid water movement and facilitates the removal of large amounts of cathode reaction water produced at high current, mitigating mass transport flooding limitations. Such substrates do not hold or retain as much water resulting in cell drying issues at

FIGURE 3. Integrated Water Content from Neutron Images During Current Transient (a) wetting from 0.5 A to 34 A, 40°C and 0/0 inlet RH (b) drying from 34 A to 0.5 A, 40°C and 0/0 inlet RH.

lower currents with low gas inlet RHs. The opposite effects apply to GDL substrates with low PTFE loadings. MPLs with less open and lower percentage pore structure behave differently with high PTFE loadings. With high loadings the MPLs act as a barrier to water flux. They are likely a barrier to gas flux, although that was not directly studied here. High PTFE MPLs can be used to prevent water loss from the membrane during dry operating conditions but they can also inhibit water moving in to hydrate the membrane. The opposite effects seem to apply to low PTFE MPLs.

Gas counter flow configuration provides more even water distribution throughout the fuel cell compared to co-flow gas configuration. With co-flow configuration, the gases, which are accumulating moisture as they pass down the channels, approach saturation conditions toward the outlet end of the fuel cell that may result in substantial condensation here. Counter flow fuel cells often result in better performance at low inlet RH conditions due to the more even water distribution.

Results: Performance and Durability of Sub-Freezing Operations

The effect of MEA and GDL structure and composition on the performance of single PEM fuel cells operated isothermally at sub-freezing temperatures was studied. The cell performance and durability are dependent on both the MEA/GDL materials used and on their interfaces. When a cell is operated isothermally at sub-freezing temperatures in constant current mode, the water formation due to the current density initially hydrates the membrane/ionomer and then forms ice in the catalyst layer/GDL. An increase in high frequency resistance was also observed in certain MEAs where there is a possibility of ice formation between the catalyst layer and GDL leading to a loss in contact

FIGURE 4. Water/ice profiles obtained after various isothermal sub-freezing operations. The profiles indicate only the ice/water formed due to the current flow at the subfreezing temperature and are referenced to the initial water content before the operation.

area. The total water/ice holding capacity for any MEA was lower at lower temperatures and higher current densities. The durability of MEAs subjected to multiple isothermal starts was better for LANL-prepared MEAs as compared to commercial MEAs, and cloth GDLs when compared to paper GDLs.

High-resolution neutron imaging performed on specially designed 2.25 cm² hardware with the Gore MEAs and paper GDLs revealed that the ice formation is concentrated in the cathode catalyst layer (Figure 4). Here the peak in the water profiles is at the MEA/cathode GDL edge for all the isothermal starts where $T = -10^{\circ}\text{C}$. Moreover, the water capacity in these operations is consistent with the standard 50 cm² cell and there is less capacity to hold water at the lower temperatures (0.99 mg/cm² at -10°C and 0.39 mg/cm² at

-19°C when operated at 0.02 A/cm²) and higher current densities (0.99 mg/cm² at 0.04 A/cm² and 0.67 mg/cm² at 0.12 A/cm² when operated at -10°C). Moreover when the cell is started from -8.5°C, the peak in water content is located within the cathode GDL, well outside of the cathode catalyst layer. Figure 4 shows water/ice profiles obtained after various isothermal sub-freezing operations. The profiles indicate only the ice/water formed due to the current flow at the subfreezing temperature and are referenced to the initial water content before the inside the cathode GDL substrate confirming that there is significant amount of water penetrating into the GDL before freezing. These results help explain the fact that the water holding capacity in these MEAs is greater than that available in the membrane and catalyst layers and why there is more degradation at the lower temperatures when the ice formation is closer to the catalyst layer. Finally the water/ice profile is also narrower at the higher current densities and lower temperatures, consistent with the lower capacity for ice formation under those conditions.

Conclusions

- The ability to measure water in situ during cell operation and relate water profiles to cell operating conditions and performance is invaluable in selecting operating conditions and designing fuel cell components for optimal water management.
 - AC impedance including HFR and neutron imaging in situ measurements correlate water concentration to performance.
- Transient measurements show hysteresis in wetting/dewetting.
 - MEA wetting is a fast process likely related to the hygroscopic nature of the membrane.
 - MEA dewetting appears to be a slower diffusion controlled process.
- Neutron imaging is successful at identifying the effect of operating conditions on water concentrations within the PEM fuel cell.
 - Different materials show different water concentration profiles.
 - More water accumulation in GDL under land area when compared with the GDL under flow channel area.
 - Counter flow keeps membrane well hydrated in comparison with co-flow.
- GDL surface properties affect water transport.
 - Greater mass transfer resistance for GDLs with higher MPL PTFE loadings.
 - Substrate Teflon[®] content does not have major role in determining water content.
- Sub-freezing operation:
 - Operation at sub-freezing temperatures builds up water (ice) in the cell, which is located primarily on the cathode side, and can penetrate into the cathode GDL depending upon operating conditions.
 - Degradation observed in the amount of active catalyst surface area (H₂ adsorption peak) was strongly dependent on the MEA.
 - Catalyst layer ice formation may be controlled and its effects mitigated by careful control of the catalyst layer morphology.

Future Directions

Experimental and Characterization

- Three-dimensional X-ray tomography during operation observing water transport in GDL pores:
 - Identify hydrophobic pores vs. hydrophilic pores.
 - Identify liquid water pathways in GDLs.
- Incorporate 3-dimensional X-ray tomography pore size distribution into capillary pressure simulation.
- Conduct segmented cell measurements varying the GDL PTFE loading as a function of cell location and with counter flow inlets configurations.
- Measure the effect of compression and GDL substrate porosity.
- Better identify GDL loss of hydrophobicity degradation mechanism.
 - Surface characterization (transmission electron microscopy) and surface species identification (diffuse reflectance infrared Fourier transform spectroscopy).
- Measure capillary pressure in GDLs with concurrent flow of water and gas.

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2. Mukundan, Rangachary and Rod Borup, **Visualizing Liquid Water in PEM Fuel Cells Using Neutron Imaging**, Accepted for Publication in Fuel Cells.
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V.B.2 Water Transport in PEM Fuel Cells: Advanced Modeling, Material Selection, Testing, and Design Optimization

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- BCS Fuel Cells, Bryan, TX
- ESI US R&D, Huntsville, AL
- Techverse, Cary, NC
- SGL Carbon, Meitingen, Germany
- University of Victoria, Victoria, BC, Canada

Project Start Date: June 1, 2007

Project End Date: May 31, 2011

Objectives

- Develop advanced physical models for water transport and generation, and conduct material and cell characterization experiments.
- Improve understanding of the effect of various cell component properties and structure on the gas and water transport in a proton exchange membrane (PEM) fuel cell.
- Encapsulate the developed models in a modeling and analysis tool for cell design and future application.
- Demonstrate improvements in water management in cells and short stacks.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) Durability
- (D) Water Transport within Stack
- (E) System Thermal and Water Management
- (G) Start-up and Shut-down Time and Energy/Transient Operation

Technical Targets

This project is addressing fundamental issues in water transport within the fuel cell stack. The resulting understanding will be applied toward the design of stack components and operating strategies that enable meeting the 2010/2015 targets for transportation fuel cell stacks operating on direct hydrogen:

- Stack power density: 2,000 W/L
- Cold start-up time to 50% rated power @ 20°C: 5 secs
- Unassisted start from low temperature: -40°C

Accomplishments

- Completed characterization of key physical and transport properties for SGL, Ballard Materials Products (BMP) and Toray gas diffusion layer (GDL) materials, including variation with polytetrafluoroethylene (PTFE) loading;
- Analyzed impact of GDL microstructure and PTFE loading on GDL permeability, wetting characteristics and water breakthrough, and capillary pressure behavior with validated micro-scale multiphase Lattice Boltzmann Method (LBM) transport models;
- Measured water droplet growth rate, dynamic contact angles, and break-away frequency during water emergence at model GDL-channel interfaces;
- Measured wet pressure drop and transient pressure signatures of two-phase flows in channels and cells to evaluate design sensitivity and support computational fluid dynamics (CFD) model development and validation; and
- Demonstrated the sensitivity of cell performance to modifications in materials and design that impact water management.

Introduction

Water management in PEM fuel cells is challenging because of the inherent conflicts between: supplying adequate water to establish and maintain the membrane electrical conductivity, removing the water produced by the electrochemical reactions at the cathode, and uniformly distributing the gaseous reactants at catalyst surfaces near the membrane to effectively utilize these costly catalysts. As power density of the cells increases, more water will be generated within the same cell volume. Therefore, increasing power density requirements will drive a greater need for design tools incorporating an improved understanding of how liquid water is transported within fuel cells. An additional barrier to widespread use of fuel cells for automotive power is the performance degradation caused when liquid water freezes within the cells. Optimizing water management to influence where the liquid water remains at shutdown is a promising path to improving cold starting capabilities and freeze-thaw reliability.

This project is intended to improve fundamental understanding of water transport within a PEM fuel cell, and capture that knowledge in design tools capable of assisting the industry to meet targets for increased power densities and improved cold-start performance. To achieve these objectives, the project is focused on developing predictive models for water transport in GDL materials, characterizing materials for model inputs and verification, implementing the resulting understanding in engineering design tools, and validating the resulting design tools against fuel cell performance data and in-situ diagnostics of water distribution within operating fuel cells.

Approach

The overall approach of the project team is integrated experimental characterization with model development and application to meet the high level objectives of improving fundamental understanding of water transport in PEM fuel cells and demonstrating improved performance. The initial focus of the experimental characterization was on measuring relevant physical and transport properties of the GDL materials typically placed between the catalyst and reactant flow channels. Diagnostic and characterization studies have transitioned to water and two-phase (water and air) fluid transport properties of GDL materials, and analysis of water transport across material interfaces and in fuel cell channels. The related modeling studies are following a similar progression, with initial emphasis on microscale simulations of single fluid and two-phase transport within GDL materials. The simulations allow us to analyze key effects such as the impact of the

microstructure and surface treatment of the solids within porous GDL materials on the two-phase water and gas transport. The knowledge gained from the materials characterization and microscale simulations is being used to develop models suitable for incorporation into an engineering design tool for fuel cell scale analysis of reactant and water transport coupled with power generation. The verification of these models and the resulting design tool will be accomplished by comparing predicted and measured effects of material and operating conditions on cell performance and water distribution within the cell. Applying our models to screen and improve water management strategies, then testing the resulting concepts in prototype fuel cells, will further demonstrate our improved fundamental understanding and validate the resulting design tools.

Results

In this second year of the research, the emphasis has been on completing analysis and model formulation for water transport in isolated cell components such as GDLs and channels, and transitioning to address transport across interfaces and in operational cells. We have gathered experimental data under controlled conditions while developing, testing, and applying related models.

We have completed the measurement of key physical and transport properties for a set of GDL materials including SGL, Toray, and BMP papers initiated in the first year of the project. The resulting database includes porosity, pore size distribution, in- and through-plane gas permeability, effective diffusivity, and electrical and thermal conductivity. For the SGL and Toray materials, a range of PTFE loadings were used to identify the response of measured properties to this common treatment. LBM simulations of gas transport through numerically generated GDL microstructures with a range of PTFE loadings, Figure 1, demonstrate good agreement with the measured variation in gas permeability. The key finding from the simulations was that the relatively simple, stochastic approach we developed for incorporating the PTFE distribution in the model structures is adequate for describing the impact of PTFE loading on transport properties in carbon paper GDL materials. The other key GDL properties utilized in continuum water transport models, capillary pressure and relative permeability, were measured to determine their dependence on water saturation. The capillary pressure measurements, Figure 2, were performed using a positive displacement technique, and in addition to capillary pressure as a function of water saturation we also were able to quantify the pressure required for water breakthrough and residual water saturation after wetting. Relative permeability is a key input property for continuum CFD-based analysis of water

FIGURE 1. Predicted and Measured Dependence of GDL Permeability on PTFE Loading, with Numerically Generated GDL Structures

FIGURE 2. Measured Capillary Pressure for Toray Paper GDL Media During Imbibing and Drainage

transport in porous media and is typically assumed to vary with water saturation cubed. The measurements indicate that a linear variation is more appropriate, although there is still uncertainty due to the challenges in specifying and controlling the water saturation while measuring air flow through the sample.

Additional water transport studies were performed to provide quantitative information on water transport in GDLs and across the GDL-channel interface. The

GDL transport studies use a system for simultaneous monitoring of the capillary flow, pressure, and injected water volume as water percolates through GDL samples. These experiments complement the relative permeability studies, and are providing improved understanding of the governing physics as water begins to percolate through and exit the GDL material. Key findings include history-dependent invasion, namely that the observed pressure required to drive a fixed volumetric flow rate increases for a previously wet sample. Image analysis is also being performed during these percolation studies, to quantify the growth and clustering of water droplets on the surface while simultaneously measuring the injected water volume and pressure. At the GDL-channel interface, detachment of water droplets to allow rapid water transport down the channel is a key process governing effective water removal. We are studying this process on controlled surfaces, with quantitative imaging, Figure 3, to determine dynamic water/substrate contact angles and correlate droplet removal frequency with flow conditions.

Model development efforts have focused primarily on the CFD-based cell-scale models. The key physical sub-models for water transport in GDLs and catalyst layers, capillary pressure and Darcy's Law resistance to flow in porous media, have been incorporated into the two-phase fluid flow solver. The resulting models have been integrated with the chemical species and electric current conservation equations to allow simulation of operational fuel cells, and integration with energy conservation is underway. These models have been evaluated for a variety of relevant test problems, primarily simplified representations of the water transport characterization experiments described above. The tests have demonstrated that the sub-models are correctly implemented and experimental trends can be reproduced, but there are still numerical stability issues and transient simulations are typically required to obtain satisfactory convergence. Ongoing efforts include evaluation of alternate models for fluid-fluid drag in channels, inclusion of surface tension effects to allow simulation of droplet formation at GDL-channel interfaces, and development of a physically based interface matching condition at the GDL-channel interface.

We have developed a fixture for measuring pressure drops and pressure profiles during two-phase flows in single fuel cell channels with the option to inject water at specific locations or distributed by a GDL. A test matrix for a range of air flow rates and water injection rates, corresponding to stoichiometric operation at current densities of 0.3, 1, 1.5, and 2 A/cm², were characterized for two channel designs. For two-phase flows in channel design 1 with water injection at a single upstream point, significant pressure transients were observed at the lowest water and air flow rates and run-to-run repeatability was also worse. The steady-state models predicted pressure drop trends with water

FIGURE 3. Apparent Contact Angles and Droplet Base Diameter Time Evolution during Single Hole Water Injection Experiment (left) and Droplet Shape Evolution (right)

FIGURE 4. Measured and Predicted Two-Phase Pressure Drop in Single-Channel Fixture at 61 sccm Air Flow with Varying Water Flow; Predicted Water Distribution for 0.011 ml/min Water Injection (inset)

flow rate variation for a given air flow relatively well, Figure 4, despite the transient nature of the system at low water flows. However, the model predictions for wet-to-dry pressure drop ratio versus overall flow rate did not produce the observed variation. For channel design 2, with a wider but shorter cross-section, the predicted wet/dry pressure drop ratio variation with total flow had worse agreement with experiment than design 1. The models are qualitatively predicting the correct water distribution in the channel, based on experimentally derived flow field regime maps, namely a horizontal stratified film as shown in Figure 4. Incorporation of gravity effects improved the pressure drop agreement in the design 1 simulations, and caused the water film to form at the lower surface of the channel.

Characterization of water management related effects in operational cells has continued, with

diagnostics based on both single cell polarization and internal resistance measurements. The impact of a variety of GDL materials on performance was assessed in small-scale fuel cells, 25 cm² active area, under self-humidified operating conditions. Performance sensitivity with PTFE treatment of the GDL was demonstrated, and a custom membrane electrode assembly (MEA) was developed with 20% PTFE in the microporous layer of carbon cloth type GDL that demonstrated better performance than both standard commercial and 5% PTFE content MEAs operated at 60°C and 1.75 air stoichiometry. The custom GDL modifications allow effective operation at higher temperatures, and consequently increased power density, without external humidification.

Conclusions and Future Directions

In the past year, we have characterized key material properties and processes governing water transport in individual fuel cell components and across material interfaces. Initial improvements of cell performance via materials modifications have been demonstrated. Modeling and simulation has been applied at the microscale to improve understanding of water transport within GDL materials, and to guide formulation of fuel cell scale multiphysics models for integrated prediction of cell performance and water management. Specific accomplishments include:

- Completed characterization of key physical and transport properties for SGL, BMP and Toray GDL materials, including variation of these properties with PTFE loading;
- Analyzed impact of GDL microstructure and PTFE loading on GDL permeability, wetting characteristics and water breakthrough, and capillary pressure behavior with experimental characterization and validated micro-scale multiphase LBM transport models;
- Measured water droplet growth rate, dynamic contact angles, and break-away frequency during water emergence at model GDL-channel interfaces;
- Measured wet pressure drop and transient pressure signatures of two-phase flows in channels and cells to evaluate design sensitivity and support CFD model development and validation; and
- Demonstrated sensitivity of cell operation to water management, and performance improvement, through materials and design modifications.

Key activities planned for the coming year include:

- Complete experimental characterization of water transport in cell components and non-operational cells to screen water management improvement concepts and provide validation data for cell-scale models;
- Complete integration of heat transfer and electrochemistry with two-phase CFD-based cell-scale models and evaluate against operational cell experimental data, improve fluid-fluid drag models and surface tension implementation for better prediction of wet channel pressure drop; and
- Devise and screen concepts for improved water management by applying the developed experimental diagnostic tools and numerical models, with initial emphasis on channel and GDL material designs for effective water removal with low pressure drop and minimized pressure transients.

Future work will consist primarily of testing the models against diagnostic data and improving them as necessary, while demonstrating an improved understanding of the key factors controlling water transport by developing improved water management approaches.

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V.B.3 Visualization of Fuel Cell Water Transport and Performance Characterization under Freezing Conditions

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Contract Number: DE-FG3607GO17018

Subcontractors:

- General Motors, Honeoye Falls, NY
- Michigan Technological University, Houghton, MI

Project Start Date: March 1, 2007
Project End Date: February 28, 2010

Objectives

- Improve fundamental understanding of the water transport processes in the proton exchange membrane fuel cell (PEMFC) stack components under freezing and non-freezing conditions.
- Optimize materials, design, and surface properties of gas diffusion layer (GDL) and bipolar plate to alleviate flooding and suppress regions of dehumidification.
- Develop experimental and modeling tools to evaluate ex situ and in situ performance of PEMFC stack components.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies (HFCIT) Program Multi-Year Research, Development and Demonstration (RD&D) Plan:

- (A) Durability
- (C) Performance
- (D) Water Transport within the Stack

Technical Targets

This project is directed at developing a better water management strategy within PEMFC stacks. Insight gained will be applied toward the design and demonstration of a robust fuel cell that meets the following DOE technical targets as outlined in the HFCIT Multi-Year RD&D Plan:

- Unassisted start from low temperature: -40°C
- Durability with cycling at operating temperature of $\leq 80^{\circ}\text{C}$: 5,000 h
- Energy density: 2 kW/L

Accomplishments

In the last year, the project team implemented changes to the baseline GDL and flow channel and explored various GDL/channel combinations with ex situ and in situ experiments. Liquid water transport in the GDL and the channels under normal and freezing conditions and during shutdown purge were mapped and quantified. Technical accomplishments during this period are listed below:

- Demonstrated that shutdown air purge is controlled predominantly by the water carrying capacity of the purge stream and the most practical means of reducing the purge time and energy is to reduce the volume of liquid water present in the fuel cell at shutdown. The GDL thermal conductivity has been identified as an important parameter to dictate water accumulation within a GDL.
- Found that under the normal shutdown conditions most of the GDL-level water accumulation occurs on the anode side and that the mass transport resistance of the membrane electrode assembly (MEA) thus plays a critically important role in understanding and optimizing purge.
- Implemented changes to the baseline channel surface energy and GDL materials and evaluated their performance with the ex situ multi-channel experiments. It was also found that the microporous layer (MPL) promotes the formation of the mist flow pattern at high air flow regimes and the formation of large slugs in the channels in the low air flow regime. Both of these two effects are related to the reduction of the water saturation and

- the number of water breakthrough locations in the GDL caused by the MPL.
- Simultaneously visualized the water transport on cathode and anode channels of an operating fuel cell. It was found that under dry hydrogen/air conditions at lower temperatures the cathode channels display a similar flow pattern map to the ex situ experiments under similar conditions. Liquid water on the anode side is more likely formed via the condensation of water vapor which is transported through the anode GDL.
- Investigated the water percolation through the GDL with pseudo-Hele-Shaw experiments and simulated the capillary-driven two-phase flow inside gas diffusion media, with the pore size distributions being modeled by using Weibull distribution functions. The effect of the inclusion of the microporous layer in the fuel cell assembly was explored numerically.
- Developed a new method of determining the pore size distribution in the GDL using scanning electron microscope (SEM) image processing, which allows for separate characterization of GDL wetting properties and pore size distribution.
- Identified a drop size dependency of the static contact angle on the GDL, which is measured using an adaptation of the classical sessile drop method and is calculated using an in-house code specially developed for measuring static contact angles on rough, porous substrates.
- Developed a unique SEM sample holder which allows for visualization of GDL material while under compression. The stress-strain behavior of the GDL sample can be obtained simultaneously. This imaging technique reveals internal damage to the GDL due to compression.

Introduction

Water management is critical to the successful implementation of PEMFCs in various industry sectors. Water management is especially challenging under low temperature conditions due to the low water carrying capacity of the reactant stream and the possibility of water freezing within the fuel cell assembly, which results in premature degradation. This project is directed at developing a better water management strategy within PEMFC stacks. To achieve these objectives, the project has been focused on the following technical issues:

- Two-phase (water and gas) transport in the fuel cell stack, including the GDL, flow channels, and their interfaces.
- Structural and surface properties of materials and how they change during operational events, such as freeze/thaw.

- Experimental and modeling tools to evaluate ex situ and in situ performance as well as local variations in current density and water distribution.

Approach

The objectives of this project will be accomplished through an iterative approach that starts at the component level, synthesizes this fundamental learning into combinatorial ex situ experiments with nearly full visual access, and then progresses to increasingly more complex in situ experiments that utilize advanced diagnostic methods such as current density, high-frequency resistance distributions and neutron radiography. The success of the project lies in new materials, improved design concepts and operating strategies. Both experimental and modeling tools will be used to evaluate ex situ and in situ performance.

Results

One of the important issues in developing efficient purge strategies relates to the location of liquid water, i.e., anode vs. cathode. It was observed that, with a fixed cathode air purge flow rate and humidity, the rate of bulk water removal is nearly independent of whether the water resides in the anode or cathode diffusion medium. This independence indicates that the purge dynamics are dominated by the relative humidity conditions of the channel-level air stream and for a given shutdown condition the purge time can only be effectively modified by changing the water vapor carrying capacity of the air purge stream. Investigation of bulk water removal was extended by measuring removal rate over small “differential” regions of the fuel cell active area where the relative humidity conditions within the channel are approximately constant. These experiments revealed a distinctly faster removal rate from the cathode side than from the anode side (Figure 1), and implied that a significant resistance was introduced by the membrane to anode water removal by the cathode air steam. Applying a similar method to the analysis of purge of water generated during in situ experiments indicates that most of the water removed by the air purge resides on the anode side of the fuel cell.

The baseline characterization revealed that shutdown purge time and energy are mainly constrained by the quantity of liquid water retained in the GDL during operation prior to shutdown. Increasing GDL thermal conductivity will effectively lower the MEA temperature and, thus, decrease the concentration gradient that drives water vapor from the electrode to the channel. The impact of GDL thermal conductivity on saturation at various operating conditions was tested. Initial results indicate that water accumulation is sensitive to thermal conductivity, especially at higher temperatures, as shown in Figure 2. This is due to the

Mass Transfer Evaluation

Requires differential evaluation where change in channel RH is less significant

FIGURE 1. Mass Transfer Evaluations on Differential Elements at the Inlet Edge of the Active Area

FIGURE 2. Impact of Thermal Conductivity on GDL Saturation at 80°C

fact that reducing saturation pressure near the MEA with an increased thermal conductivity GDL effectively brings the condensation front deeper into the GDL, resulting in higher steady state liquid water content.

Freeze start experiments were conducted with the baseline fuel cell system. It was observed that the freeze start at -20°C from a shut-down condition with 15 seconds air purge or less fails due to the complete blockage of reactant flow paths caused by the ice formation at the end of the bipolar plate and at the channel-to-manifold transition region. However, with longer shutdown air purges, it was possible to generate power for some period until the voltage fell below 200 mV (presumably due to ice filling the electrodes).

Changes to the baseline channel surface energy were implemented by treating the channel with a hydrophilic coating ($\theta \sim 11^{\circ}$) provided in-house by General Motors and the effects of this change on the two-phase flow in channels were studied. The hydrophilic channel was found to facilitate the removal of liquid water compared to the case of non-treated channels ($\theta \sim 60^{\circ}$) (Figure 3). For the hydrophilic channels, the transition line of slug/film patterns is significantly shifted toward lower air velocities, indicating the reduced slug formation tendency. It was found that the MPL promotes the formation of not only the mist flow pattern but also large slugs in the channels. This is ascribed to the role of the MPL which reduces the water saturation and limits the water breakthrough locations in the GDL which is predicted numerically as shown in Figure 4.

During the in situ fuel cell experiments with visualization on both cathode and anode it was found that, under dry hydrogen/air conditions at lower temperatures (35°C in this study), the cathode channels display a similar flow pattern map to the ex situ experiment at similar conditions, as expected. On the anode side it was found that: i) anode liquid water formation occurs largely due to condensation of water vapor which is transported through the anode GDL; ii) the greatest liquid water activity was observed downstream, similar to that observed in the cathode channels, indicating a transition point from single- to two-phase flow along the channels; and iii) the water content in the anode channels decreases and the water content in the cathode channels increases as current density increases.

The pseudo-Hele-Shaw experiments on GDLs demonstrate the importance of drainage transport mechanisms which are not properly accounted for in current transport models of PEMFCs. A two-dimensional numerical model (see Figure 4) was developed to study drainage transport in the GDL. Five contact angles and six pore size distributions for a GDL with an MPL were studied. The contact angle affects the percolation pressure, but not the saturation curve. The average pressure at which the water percolates through

FIGURE 3. The two-phase flow pattern map for (a) hydrophilic channel and (b) non-treated channel tested with baseline GDL in the ex situ multi-channel test apparatus.

FIGURE 4. Numerical simulation of water transport in the cathode. Water distributions are shown (c) without an MPL and (d) with an MPL when liquid water first enters the flow channel. Blue represents water, white represents air, and black represents the fiber structure of the diffusion media.

the gas diffusion layer decreases as the average pore size increases. The effect of the MPL is to reduce the amount of water in the GDL which enhances capillary fingering and subsequently facilitates reactant transport to the catalyst layer. The presence of the MPL also results in a high pressure in the catalyst layer forcing the anode and cathode catalyst layers and the PEM to be fully saturated with water (see Figure 4).

Static contact angle measurements have shown the contact angle of water on GDLs to be dependent on the material, the temperature and the drop size. As the drop size decreases, so does the static contact angle. The drop size dependence of the contact angle has been previously reported on polymeric substrates. The effect is exacerbated on the GDLs most likely due to the drop deposition method as well as the rough, porous surface and the poly-tetrafluoroethylene coating.

A new model for predicting the morphology of water in the flow field has been developed using *Surface Evolver*. A parametric study of the critical volume at which a liquid drop will transform spontaneously into a liquid plug in a channel has been completed for variations in the channel bend dihedral, channel contact angle and GDL contact angle. This model can be used to predict the rate of liquid plug formation for a given current density and flow field configuration.

Statistical analysis of GDL images taken in a SEM has been shown to provide information on distributions of pore size, pore shape, pore orientation, and nearest neighbors. In addition, stereo SEM imaging allows for determining of the distribution of pore depth and volumes. The SEM image analysis has the potential to replace traditional porosimetry techniques for characterizing GDLs.

Conclusions and Future Directions

In the last year, changes to the baseline GDL and flow channel were implemented and the performance was evaluated with ex situ and in situ experiments. GDLs with lower thermal conductivity and channels with hydrophilic coating have been demonstrated to facilitate the water removal and decrease the water accumulation in fuel cells. Water accumulation locations and water removal dynamics during shutdown purge have been clarified. New developments in advanced techniques, including a new printed circuit board device and SEM image analysis of GDL morphology, have provided new insight into the water distribution and transport inside a fuel cell.

A key contribution from the previous studies is that the time and energy needed for liquid water removal during cathode purge is predominantly controlled by the volume of liquid water present at shutdown. Thus, in the future, the new material and design set selection will focus on changes which are expected to

minimize the accumulation of water during steady-state operation. These directions include i) GDLs having lower thermal conductivity and thinner thicknesses (it is reasonably assumed that thinner GDL will have less water accumulation), ii) the flow field material with significantly increased or decreased surface energy, which are to favor formation of either liquid films that can be removed via evaporation, or smaller slugs that can be more easily removed by gas shear, and iii) the channels with geometric features that are more representative of full-size automotive hardware, including stamped metal and molded carbon composite bipolar plates.

The numerical simulation will be expanded to study the effects of cracks on microporous layer as well as to study the effect of mixed wettability (wetting and non-wetting) porous on the gas diffusion media. The ex situ pseudo-Hele-Shaw experiments will be performed on different gas diffusion layers in order to classify them depending on their wettability and morphological properties. The experimental data obtained from this ex situ experiment will be used to validate the numerical simulation through non-dimensional analysis. The sensitivity of pore size distribution data obtained from SEM image analysis, as characterized by the Weibull distribution parameters, to magnification and large pore size cutoff will be studied. The results of this study should allow for a standardization of the technique for characterizing GDL morphology.

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V.C.1 Effects of Fuel and Air Impurities on PEM Fuel Cell Performance

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Project End Date: October, 2011

the experimental determination of the limits of impurity tolerance within those technical targets. The results of this project will provide data for defining the fuel cell hydrogen fuel specifications and intake air quality and assess the role of impurities in fuel cell performance degradation.

TABLE 1. Technical Targets: Electrocatalysts for Transportation Applications (Extracted from Table 3.4.12, Technical Plan, April 27, 2007)

Characteristic	Units	2005 Status		Stack Targets	
		Cell	Stack	2010	2015
Platinum group metal total content (both electrodes)	g/kW (rated)	0.6	1.1	0.3	0.2
Platinum group metal (PGM) total loading	mg PGM/cm ² electrode area	0.45	0.8	0.3	0.2

Objectives

- Investigate effects of impurities on catalysts, membranes and other fuel cell components.
- Understand the effect of catalyst loadings on impurity tolerance.
- Investigate the impacts of impurities on catalyst durability.
- Develop methods to mitigate negative effects of impurities.
- Develop models of fuel cell-impurity interactions.
- Determine impurity tolerance limits in view of the technical targets for catalyst loading, performance and durability.
- Provide experimental data to hydrogen suppliers for defining fuel specifications.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

(A) Durability

Technical Targets

The technical targets for catalyst loading are indicated in Table 1. These targets were formulated with the assumption that fuel cell performance will not be degraded by fuel and/or air impurities or contaminants. One of the specific goals of this project is

Accomplishments

- Demonstrated common hydrocarbons, methane, ethane and propane, at PPM concentrations, do not impact fuel cell performance.
- Established that 5 ppm SO₂ in air decreases fuel cell performance of low-loading thin-ionomer proton exchange membrane fuel cells (PEMFCs).
- Confirmed that 5 ppm NO₂ in air decreases fuel cell performance however fuel cells recover quickly after exposure.
- Demonstrated ammonia reacts with membranes to form NH₄⁺.
 - Measured very low electrochemical oxidation rate in acidic conditions.
 - Demonstrated removal is via ammonium ion-aqua ammonia equilibrium.
- Validated cation impurity models they explain why low levels of ionic contaminants can cause significant performance losses.

Introduction

Fuel cells efficiently convert flows of chemical energy to electrical power. Fuel cell performance can be severely impacted by contaminants or impurities that decrease the electrochemical catalytic rates, interfere with proton transport across the polymer electrolyte, or impede the flow of reactants to/or reaction products away from the anode or cathode charge transfer interfaces. The platinum metal catalyst surfaces may

be deactivated by strongly adsorbing species such as sulfur containing molecules and carbon monoxide. The strongly adsorbing species both block surface sites for catalytic activation and alter the electronic structure of the surface decreasing charge transfer rates. Positively charged contaminant ions often times have much greater chemical affinity to the ion transport sites within the polymer than protons. The foreign cations typically have lower mobilities than protons and reduce ionic conductivity. The presence of impurities may also decrease the operational lifetime of the fuel cell by decreasing performance irreversibly to an unacceptable value or by increasing component failure rate.

Approach

Our approach to understanding impurity interactions with fuel cell components utilizes both experimental and modeling efforts. We perform fuel cell performance measurements in the presence of introduced impurities and follow the measurements with electro-analytical diagnostic methods such as adsorbate stripping voltammetry and alternating current (AC) impedance spectroscopy. Post-experimental analysis includes trace level chemical analysis of fuel cell components and effluent water, electron microscopy and X-ray diffraction. We also experimentally determine impurity thermodynamic behavior (ion-exchange and water activity coefficients) and transport properties such as membrane permeability and ionic conductivity.

Theoretical studies include computer models of impurity interactions with anode and cathode electrocatalysis. We also model the effects of foreign cations upon fuel cell performance. The modeling results are validated with experimental measurements such as hydrogen pump experiments and X-ray and electron beam microscopy of impurity distribution.

Results

Sulfur compounds are well known electrode catalysis poisons, however tolerable impurity levels at low Pt catalyst loading have not been yet determined. The most prevalent sulfur-containing air species is sulfur dioxide from fossil fuel combustion. The Department of Energy future targets call for a decrease in anode and cathode Pt loading. We evaluated the response of a 50 cm² fuel cell (Nafion® NRE212) to 5 ppm SO₂ in air (2.0 stoichiometry) injection at the cathode inlet past the humidification system (100% saturation). Figure 1 illustrates the results of a fuel cell test run at constant current 0.8 A/cm² (H₂ at 1.2 stoichiometry). The fuel cell operating voltage at constant current decreased rapidly with approximately 50% recovery after sulfur dioxide injection was terminated. The sensitivity of the oxygen reduction reaction to sulfur is evident from this experiment. Stripping voltammetry indicates a Pt-S

FIGURE 1. Effect of 5 ppm Sulfur Dioxide Injection to Fuel Cell Cathode Air Stream (80°C, 100% relative humidity)

species similar in redox behavior to species formed by introduction of hydrogen sulfide or sulfide ions. High ambient air concentrations of sulfur dioxide will continue to be a barrier for the introduction of fuel cells in the industrialized urban areas of highly polluted developing countries such as China.

Another common class of emission species from fossil fuel combustion systems are oxides of nitrogen. High combustion temperatures and pressures promote the reaction of nitrogen with air to form these acid gases. We studied by cathode injection, the effects of 5 ppm nitrogen dioxide, into an operating fuel cell similar to the one used for the sulfur dioxide experiments. The relatively humidity was also varied to assess the effects of the water vapor partial pressure on the poisoning reaction. Figure 2 illustrates the loss of cell voltage at constant current operation. The cells recover quickly from the introduction of nitrogen dioxide. Nitrogen dioxide may be reduced to nitrogen oxide on the cathode; the nitrogen oxide may be further reduced to ammonia on the anode. An alternate mechanism is the nitrogen dioxide may be rapidly reacting with water to form highly soluble nitrate ions. At high relatively humidity, free water is available to carry nitrate ions or ammonia away from the fuel cell interfaces. The fuel cells are poisoned less and recover faster when saturated humidification conditions are used as seen in Figure 2.

Ammonia is present as an impurity in hydrogen fuel from reforming and as an air impurity from the decomposition of urea and agricultural activities. Ammonia reacts strongly with protons in the perfluorsulfonic acid membrane, forming ammonium cations and increasing the pH of the membrane.

FIGURE 2. Effect of 5 ppm Nitrogen Dioxide Injection into Fuel Cell Cathode Air at Varying Relative Humidity: 100, 75, and 50% @ 80°C

A decrease in membrane acidity shift fuel cell open circuit potential, decreases fuel cell electrocatalytic rates and reduces proton conductivity.

It is therefore expected that ammonia introduced from either the fuel or air side, will severely impact polymer fuel cell performance. Figure 3 displays the effect of 1 ppm ammonia introduction into a PEMFC for varying time periods. The impact on the polarization curve is substantial; the kinetic, ohmic and mass transport portions of the polarization curves are negatively impacted by the presence of ammonia.

Ammonium oxidation and/or dissolution into product water are two possible removal/recovery mechanisms. Ammonium oxidation was studied by introduction of a 0.1M $\text{NH}_4(\text{SO}_4)$ solution into a 5 cm^2 Nafion® 117 PEMFC anode compartment. A small ammonia oxidation current, $<10^{-3}$ A/ cm^2 above 0.6 V was detected by sweep voltammetry. The oxidation current was very low, probably too small to account for fuel cell recovery. The aqua-ammonia water reaction equilibrium is the more significant mechanism of ammonia removal.

Electrochemical modeling continues to clarify why relatively small quantities of foreign cations produce a large negative effect on fuel cell performance. A model was developed by Kienitz using concentrated solution theory to describe the one-dimensional ammonia impurity profiles as a function of current density. The slow removal rate of foreign cations coupled with lower mobilities than protons was shown to produce non-uniform impurity profiles. The concentration ratio of protons to impurity ions decreases from anode to cathode when current spontaneously flows in the fuel

FIGURE 3. Effect of 1 ppm Ammonia Injection to the Cathode for Varying Times (100% relative humidity, 80°C)

cell. Increasing the current density decreases the proton concentration in the cathode leading to decreased proton transport to the oxygen reduction inhibiting fuel cell performance. However our ammonia poisoning experiments show impacts to performance in both electrokinetic and mass transport segments of the fuel cell polarization curve. We suspect that foreign cations are also changing the water concentration in the electrode layer. Reducing the water content of the ionomer at the reaction interface will decrease the oxygen reduction kinetics and will decrease the proton conductivity of the ionomer (catalyst layer sheet resistance). We will probe water and ion profiles simultaneously within the electrodes in future model refinements.

Conclusions and Future Directions

Experimental measurements and theoretical modeling has increased our understanding of impurity effects in low temperature fuel cells. We now possess a much better understanding of how impurities fundamentally interact with fuel cells, particularly ions that substitute for protons within the electrolyte. We need to further understand the impurity removal processes and kinetics. Our future work will:

- Improve understanding of SO_2 interaction with Pt using cyclic voltammetry coupled with gas chromatography and mass spectroscopy.
- Improve understanding of membrane N speciation via spectroscopy and determine tolerance as a function of cathode loadings at various conditions.
- Membrane transport studies, water equilibrium studies and fuel cell testing of loss rates.
- Model water activity effects upon electrode kinetics.

- Extend model to analyze slowly diffusing divalent metal cations.
- Perform neutron imaging at the National Institute of Standards and Technology to determine cation-impurity effects on water transport.
- Future in situ imaging of impurities in operating fuel cells by X-ray tomography.

FY 2009 Publications/Presentations

1. Garzon, F.; Uribe, F., Impact of Fuel Contaminants On Fuel Cell Performance. In *Handbook of Fuel Cells*, Gaistiger, H., Ed. J. Wiley and Sons: London, UK, 2009.
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4. Garzon, F.H.; Lau, S.H.; Chang, H.; Tkachuk, A.; Feser, M.; Yun, W.; Chiu, W.K.S., Non-invasive, multiscale 3D x-ray characterization of porous functional composites and membranes, with resolution from MM to sub 50 NM. In *2008 MRS International Materials Research Conf.* ; 9-Jun-08 ; Chongqing, China, Chongqing, China, 2008.
5. Garzon, F.; Uribe, F.; Rockward, T., Fuel and Air Impurity Effects in Fuel Cells. In *Gordon Research Conference Fuel Cells*, Mench, M.M., Ed. Bryant College, Smithfield RI, 2008.
6. Einsla, M.; Mukundan, R.; Brosha, E.L.; Garzon, F.H., New Synthesis Routes for Indium-Doped Tin Pyrophosphate Proton Conductors. *ECS Transactions* 2008, 16 (2), 2165-2170.
7. Brosha, E.L.; Rockward, T.; Uribe, F.A.; Garzon, F.H., Qualitative Determination of H₂S Crossover Rates in Nafion Membranes using Ion-probe Techniques. *ECS Transactions* 2008, 16 (2), 1205-1217.

V.C.2 Fundamental Effects of Impurities on Fuel Cell Performance and Durability

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Contract Number: DE-FG36-07GO17011

Subcontractors:

- Savannah River National Laboratory, Aiken, SC
- John Deere, Charlotte, NC

Start Date: February 15, 2007

Projected End Date: February 14, 2010

Objectives

- Investigate the effect of impurities in the hydrogen fuel streams on the operation and durability of fuel cells. These impurities include water, hydrocarbons (including formaldehyde, formic acid), oxygen, inert gases (He, N₂, Ar), CO₂, CO, sulfur-containing gases, ammonia, halogenated compounds and particulates.
- Propose mechanisms for how impurities in the hydrogen fuel stream affect the components of the fuel cell catalyst and polymer membrane.
- Determine strategies to reduce the poisoning effect of these impurities.
- Disseminate findings so that they are available to other members of the DOE Hydrogen Quality team and to FreedomCAR technical teams.

Technical Barriers

This project addresses the following technical barrier from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

(A) Durability

Technical Targets

This project is addressing fundamental research into effects and mechanisms of impurities on the performance and durability of polymer electrolyte membrane (PEM) fuel cell systems. The activity broadly supports the following technical targets established by DOE:

- Transportation Fuel Cells
 - Durability with cycling: 5,000 h by 2015
- Stationary PEM Fuel Cell Power Systems:
 - Durability @ <10% rated power degradation: 40,000 h by 2011

Accomplishments

- Determined that there is significant H spillover from Pt to the carbon support at fuel cell conditions ($\approx$ H coverage of Pt).
- Measured the degree that CO poisoning in the range of 10-70 ppm decreases H₂ activation, hydrogen chemisorption, and H spillover on Pt/C.
- Calculated surface coverage of CO indirectly from hydrogen surface concentration measurements and directly from temperature-programmed desorption (TPD) results in the range of 70-500 ppm on Pt/C, which indicated a maximum CO coverage of approximately 42%.
- NH₃ and inert gases (N₂, Ar, and He) were determined not to have an effect on H₂ activation on Pt/C.
- It was found that CO, CO₂, perchloroethylene (PCE), acetaldehyde, tetrahydrofuran (THF), and ethylene did not affect the conductivity of Nafion[®] membrane and the proton availability of Nafion[®] components (membrane and Nafion[®] supported on Pt/C).
- However, 1 ppm PCE in the H₂ fuel was found to decrease fuel cell current by 90% at 0.6 V in less than 15 hours. This appears to be a result of Pt poisoning. Even at 50 ppb, the current International Organization for Standardization (ISO) limit, PCE was found to be detrimental to fuel cell performance.

- The effect of NH_3 on the conductivity of Nafion[®] was measured to be a strong function of relative humidity (RH), with a reduction in conductivity of 3.4X at 100% RH, but 50X at 30% RH. Poisoning also occurs at a slower rate at higher %RH.
- NH_3 poisoning at 80°C was found to cause significantly less decrease in fuel cell performance than at 60°C, but poisoning kinetics were faster.
- NH_3 was shown to cause a significant decrease in fuel cell performance at 2 ppm. Testing will be conducted to determine effects at 0.1 ppm at 60°C and 80°C per a request by DOE - Bryan Pivovar at the National Renewable Energy Laboratory together with Jim Ohi and Gerald Voecks (DOE consultants for fuel quality efforts) who are charged with defining testing priorities for all the national laboratories for the October 2009 ISO meeting. The priority for SRNL is to test the effect of NH_3 at low concentration.
- Foreign cations (Na^+ , Ca^{2+} , and Fe^{3+}) were found to have a more detrimental effect on the conductivity of Nafion[®] membrane than ammonia. At 80°C, the conductance declined by a factor of 6 and 125 at 100% RH and 30% RH, respectively.
- Esterification was validated to be a simple and convenient technique to quantitatively determine the proton availability of Nafion[®] components under fuel cell operation conditions.
- PCE has been shown to be detrimental to fuel cell performance even at the 50 ppb, the current ISO limit.
- SRNL has developed a permeation tube impurity generator to facilitate testing at DOE ISO hydrogen quality standard limits.

Introduction

PEM fuel cells show significant potential to enable efficient, clean power for stationary and transportation applications; however, the present-day technology falls short of meeting the necessary product performance and durability requirement standards. An important limitation in the operational life of PEM fuel cells is caused by the presence of hydrogen-feed stream contaminants (e.g., ammonia, carbon monoxide, etc.). These contaminants degrade the functionality of ion exchange groups within the electrolyte, degrade catalyst activity, and result in a degradation of the overall fuel cell efficiency and operational performance.

Approach

This project is a unique combination of phenomenological studies (at Clemson University) and

fuel cell membrane electrode assembly (MEA) durability testing at SRNL, with MEAs tested at SRNL composed of the same/similar materials as being investigated at Clemson. By determining the effect of impurities on the component parts of an MEA as well as overall fuel cell performance, a comprehensive mechanism of poisoning can be proposed which should suggest means to diminish that effect. Development of an integrative model is also being undertaken. The fuel cell team at SRNL is integrated into the U.S. Fuel Cell Council Joint Hydrogen Quality Task Force (JHQTFF), presently engaged to address the ISO TC 197: Hydrogen Fuel – Product Specification: Proton exchange membrane (PEM) fuel cell application for road vehicles.

Results

Phenomenological and fuel cell investigations at Clemson University and SRNL have expanded our knowledge of the MEA materials and the interactions between them and CO , NH_3 , CO_2 , PCE, acetaldehyde, THF, ethylene, N_2 , Ar, He, Na^+ , Ca^{2+} , and Fe^{3+} . CO , CO_2 , PCE, acetaldehyde, THF, and ethylene were found to have minimal effect on Nafion[®] conductivity. NH_3 and inert gases N_2 , Ar, and He have been found to have a minimal effect on H_2 activation on Pt/C other than as diluents. CO_2 has been shown to minimally affect fuel cell performance other than as a diluent.

Direct measurement of the hydrogen surface concentration on Pt/C has been able to be made with a variation on H_2 - D_2 reaction. It was found that, in the absence of CO , the surface concentration of hydrogen was approximately double that of total Pt sites available, most likely due to hydrogen spillover. However, introduction of even 10 ppm CO decreased the hydrogen surface concentration by approximately 64%. Due to the reversibility of CO adsorption and, especially, its low concentration, the time for equilibrium/steady-state CO surface coverage on Pt/C scaled proportionally to CO concentration (Figure 1).

Using TPD to study the amount of CO on the poisoned Pt/C, it was found that the total amount of CO plus hydrogen on the surface equaled that of only the total number of Pt sites available. This appears to suggest that, in the presence of CO , hydrogen spillover is severely limited.

Measurements of hydrogen surface concentration were made on Pt/C samples with different average particle sizes (Pt/C-3 [3 nm] and Pt/C-4 [4 nm]). Due to a decrease of approximately 36% in metal dispersion and 30% in metal surface area, the amount of hydrogen on Pt/C-4 was approximately half that of Pt/C-3. However, reduction in hydrogen surface concentration, in the presence of CO , was found to be similar for both catalysts (Table 1).

FIGURE 1. Surface concentration of hydrogen measurements on 100 mg Pt/C-4 as a function of time and CO concentration at 80°C and 2 atm.

The time-on-stream conductivities of Nafion® membranes (NRE-211s) in the presence of ppm NH_3 concentrations at various humidities and 80°C were determined using electrochemical impedance spectroscopy (EIS). The ionic conductivity of Nafion® is affected by the operating conditions (temperature and humidity), ammonium composition, and ammonium distribution in the membrane. The conductivity linearly decreases with time-on-stream (figure not shown) and reaches the same plateau regardless of the partial pressure of ammonia under similar conditions. The final conductivity is a strong function of humidity (see Figure 2). For the same ammonium content, uniformly poisoned membranes yield lower conductivities than non-uniformly contaminated membranes.

The real time conductivity of the Nafion® membrane during impurity exposure under practical fuel cell

FIGURE 2. Conductivity of N-211 in the protonic and ammonium forms at different humidities and 80°C.

conditions was investigated. It was found that the time-on-stream conductivity after exposures to 5% CO, 5% CO_2 , 5% ethylene, 500 ppm PCE, 500 ppm acetaldehyde, or 500 ppm THF was constant over 24 h.

The conductivities of Nafion® membranes pre-contaminated with known amounts of cations (Na^+ , Ca^{2+} , and Fe^{3+}) at various humidities were examined. The results show that the conductivities of Nafion® containing different cation ions are similar at the same cationic composition and same conditions. The effect of cations on the Nafion® conductivity appears to be more dramatic than that of ammonia. The conductance in the protonic form is 6X higher than that in the cationic form at 100 % RH, and 125X higher at 30 % RH.

SRNL has been involved in ongoing discussions with Bryan Pivovar, Chad Blake, and the Hydrogen Quality working group to determine the testing schedule,

TABLE 1. Time on stream results of hydrogen surface concentration of Pt/C-3 and Pt/C-4 in the absence and presence of CO at 80°C and 2 atm.

Sample	CO Conc. (ppm)	Hydrogen Surface Concentration ($\mu\text{mol H/g cat}$)					Total Percent Decrease in Surface H Conc.*
		0 hrs	3 hrs	6 hrs	12 hrs	24 hrs	
Pt/C-3	No CO	588	-	-	-	532	-
	70	585	-	-	-	215	63.3%
	500	636	-	-	-	226	64.5%
Pt/C-4	No CO	291	-	-	265	265	-
	10	273	214	172	123	111	59.3%
	30	289	146	110	105	99	65.7%
	70	286	107	103	97	97	66.1%

*Calculated by:
$$\frac{(\text{Surface H})_{\text{No CO}} - (\text{Surface H})_{x \text{ ppm CO}}}{(\text{Surface H})_{\text{No CO}}}$$

conditions, and MEAs to get the data needed for hydrogen fuel quality work. For this work, SRNL will be focusing on NH_3 poisoning experiments at the ISO limits at various temperature and humidity conditions. Clemson will be investigating the thermodynamic equilibrium of NH_3 with Nafion[®] at concentrations of ammonia approaching the ISO limits at different temperatures and relative humidities. Fuel cell tests are underway to measure a baseline (1,000 h) and the effect of 0.1 ppm poisoning at 60°C and 50/50 % RH with an Ion Power MEA to determine the impact of NH_3 at the ISO limit.

Impurity fuel cell tests have been performed at SRNL with PCE to characterize the performance effects that chlorinated cleaning agents (PCE concentrations of 30 ppm, 1 ppm, and 0.05 ppm) can have on fuel cell performance for anode/cathode relative humidities of 100%/50% RH (see Figure 3). The 50 ppb concentration is the ISO total limit for halogenated compounds in the hydrogen stream.

After poisoning with PCE, polarization curves were performed in the hydrogen stream to understand how PCE affected the system at different potentials. As seen in previous experiments, the cell did not recover from poisoning during operation in neat hydrogen. However, the cell did recover after cyclic voltammetry on the anode. After recovery in hydrogen was attempted, the cell was purged and cyclic voltammetry was performed on the anode. Figure 4 shows the first and second cycles of cyclic voltammogram (CV) experiments after the PCE poisoning at 1 ppm. The initial CV showed a notable oxidation peak for PCE at 0.8 V not present in baseline scans. EIS experiments on the cell showed that the membrane resistance was unchanged from the value before poisoning. This preliminary analysis suggests that PCE poisons the catalyst and not the membrane surface.

Thus, fuel cell results have shown that halogenated hydrocarbons can cause rapid degradation of fuel cell

FIGURE 3. Effect of perchloroethylene concentration on PEM fuel cell performance at 60°C.

FIGURE 4. Cyclic Voltammograms of the fuel cell anode after poisoning with 1 ppm of PCE.

performance even at the ISO standard concentration of 0.05 ppm PCE. SRNL will be working with hydrogen producers to identify other halogenated compounds such as heat transfer fluids that should be studied as part of the evaluation of halogenated compounds for the ISO standard. It is recommended that the ISO standard be amended to exclude halogenated hydrocarbons such as PCE or place a more stringent limit on the concentration of this class of compounds. It is likely that other chlorinated alkenes such as trichloroethylene, dichloroethylene, and chloroethylene would also need to have a reduced fuel quality limit.

Conclusions

Overall results to date can be summarized as shown in Table 2.

TABLE 2. Summary of Impurities Investigated

MEA Component	Poisons	No Effect
Pt	CO, PCE	NH_3 , CO_2 , N_2 , He, Ar
Nafion [®] Membrane	NH_3 , Na^+ , Ca^{2+} , and Fe^{3+}	CO, CO_2 , PCE, acetaldehyde, THF, and ethylene

At 80°C, there is a significant spillover of hydrogen onto the carbon support for Pt/C equivalent in amount to that chemisorbed on the Pt. The presence of CO, even at concentrations as low as 10 ppm, appears to prevent this. Approximately 42% of the Pt surface is covered by CO for 30 ppm concentrations and higher and this appears to be the saturation coverage in the presence of large quantities of hydrogen.

The presence of low concentrations of ammonia reduces the conductivity of the Nafion[®] membrane by a factor of 3.4-50 depending on the % RH with

the greatest reduction at lower humidities. Results for ammonia poisoning measured in liquid phase can be significantly different from results measured in the gas phase. Also, distribution of the NH_4^+ ions in the membrane can affect conductivity. Thus, even for the same amount of NH_4^+ ions overall, a uniform distribution manifests a different conductivity than a non-uniform distribution.

The presence of the metal ion impurities Na^+ , Ca^{2+} , and Fe^{3+} poison the Nafion® membrane even more than ammonia. The poisoning effect is also a strong function of RH.

Fuel cell results for 0.05-30 ppm of PCE have shown that halogenated hydrocarbons such as PCE are detrimental to fuel cell performance even at the ISO limit of 0.05 ppm. The effect seems to be mainly on the Pt catalyst.

Fuel cell tests are underway at SRNL to determine long term fuel cell behavior at the ammonia limit of 0.1 ppm. Fundamental measurements of ammonia uptake at this concentration are also planned at Clemson.

Over the coming year, measurements of the effects of ppm levels of ethylene, PCE, and CO on hydrogen surface coverage of Pt/C as a function of % RH will be carried out. The impact of Nafion® on the catalyst on these effects will also be ascertained.

FY 2009 Publications/Presentations

1. "Esterification as a Diagnostic Tool to Investigate the Proton Activity of the Nafion Components of a PEMFC," poster presentation, Southeastern Catalysis Society 7th Annual Fall Symposium, Asheville, NC, September 28-29, 2008 (Kitiya Hongsirikarn, Jack Zhang, James G. Goodwin, Jr., and Scott Greenway).
2. "The Effect of Low Concentration CO on H_2 Activation on Pt/C," poster presentation, Southeastern Catalysis Society 7th Annual Fall Symposium, Asheville, NC, September 28-29, 2008 (Jack Zhang and James G. Goodwin, Jr.).
3. "Effects of Impurities on Fuel Cell Performance and Durability," oral presentation, 2009 Annual Dept. of Energy Hydrogen Program Review Meeting, Washington, D.C., May, 2009 (James G. Goodwin, Jr., Jack Zhang, Kituya Hongsirikarn, Hector Colon-Mercado, Scott Greenway, and Peter Finamoore).
4. "The Effect of Low Concentrations of CO on H_2 Activation on Pt/C," poster presentation, 21st North American Meeting of the North American Catalysis Society, San Francisco, CA, June 5-10, 2009 (Jack Zhang, Kituya Hongsirikarn, and James G. Goodwin, Jr.).
5. "Influence of Ammonia on the Conductivity of Nafion Membranes," *Journal of Power Sources*, 195 (2010) 30-38 (Kitiya Hongsirikarn, Jack Zhang, James G. Goodwin, Jr., Scott Greenway, and Stephen Creager).

V.C.3 Effects of Impurities on Fuel Cell Performance and Durability

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Contract Number: DE-FG36-07GO17020

Subcontractors:

- FuelCell Energy, Inc., Danbury, CT
- United Technologies – Hamilton Sundstrand, Windsor Locks, CT

Project Start Date: March 1, 2007

Project End Date: February 28, 2011

Objectives

- Identify the specific contaminants and contaminant families and their concentrations present in the fuel stream.
- Develop analytical chemistry protocols and tools to detect the nature and fate of contaminating species within fuel cells.
- Determine through controlled laboratory experimentation and literature study the main drivers for voltage decay.
- Develop contaminant analytical models and computer simulations that explain and predict these effects.
- Validate contaminant models through single cell experimentation using standardized test protocols.
- Develop and validate novel technologies for mitigating the effects of contamination on fuel cell performance.
- Disseminate results through outreach activities.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section (3.4.4) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

(A) Durability

Technical Targets

This project is conducting fundamental research into the effects of impurities on fuel cell performance and durability. This activity broadly supports the following technical targets established by DOE:

- By 2010, develop a 60% peak-efficient, durable, direct hydrogen fuel cell power system for transportation at a cost of \$45/kW; by 2015, a cost of \$30/kW.
- By 2011, develop a distributed generation polymer electrolyte membrane (PEM) fuel cell system operating on natural gas or liquefied petroleum gas that achieves 40% electrical efficiency and 40,000 hours durability at \$750/kW.

Accomplishments

Hydrocarbon Testing

- Completed testing of acetaldehyde and formic acid up to a concentration of 100 ppm showing little effect of acetaldehyde on fuel cell performance but a significant effect of formic acid on fuel cell performance.
- Developed a better understanding of membrane electrode assembly (MEA) variability and the effects of this factor on impurities testing.
- Developed analytical procedures for evaluating concentrations of acetaldehyde, formic acid, and formaldehyde in the fuel stream.
- Developed mixing protocols for injecting specific concentrations of acetaldehyde, formic acid and formaldehyde into the fuel stream.

Other Impurities

- Evaluated effects of pertinent cations on the physio-chemical properties of Nafion®.
- Completed testing of cells with various concentrations of ammonia in the fuel stream.
- Developed a multi-dimensional model predicting the effects of cationic contaminants on PEM fuel cells.

Introduction

PEM fuel cells show significant promise in providing efficient, clean power for stationary and transportation applications. The technology has shown limitations relative to long-term durability goals, particularly with regard to the operational lifetime of MEAs. One of the key causes for this is the introduction of impurities into the fuel stream that impacts the functionality of ion exchange groups within the electrolyte, degrade catalyst activity, and function as diluents causing the cell voltage to degrade.

The initial technical issues being addressed concern the identification of contaminant species located in the fuel stream that may have an effect on overall fuel cell performance, and evaluation of these effects against standard test protocols. The U.S. Fuel Cell Council in conjunction with Japanese Automobile Research Institute and others have been developing hydrogen quality standards as well as procedures for contaminant testing of PEM fuel cells. These studies provide the background and basis for the initiation of our research.

Approach

This project is mainly focused on the experimental determination of the effects of key contaminants on the performance of PEM fuel cells. Experimental data collected from formalized test protocols will be leveraged to create mathematical models that predict the performance of PEM fuel cells that are exposed to specific contaminant streams. These models will be validated through laboratory experimentation and will be utilized to develop novel technologies for mitigating the effects of contamination on fuel cell performance. Results will be publicly disseminated through papers, conference presentations, and other means.

In addition, the effects of cationic impurities on the fundamental physio-chemical properties of perfluoroionomer membranes are being evaluated. Membrane samples are processed and exposed to fixed concentrations of cation salts. These samples are then evaluated with regard to gas/water crossover, ionic resistance, water content, and mechanical properties.

Results

Hydrocarbon Impurities – Based on input from working groups and industry, our team has focused our efforts on the evaluation of hydrocarbons and halogenated compounds using very specific test protocols developed as part of a multi-laboratory collaborative effort. Our strategy is to evaluate molecules that may be present in a candidate hydrogen fuel stream in order to

evaluate the effects of functionality and molecular size (e.g., number of carbon atoms).

In support of this, our team has developed techniques to prepare accurate mixtures of impurities in hydrogen and to determine the level of impurities entering the fuel cell through the hydrogen stream. A gas chromatograph has been utilized to characterize both the mixtures entering the fuel cell and those exiting the fuel cell in an effort to assess accumulation and reaction of impurity species within the fuel cell reactor. While previous studies by our group have focused on the evaluation of either gaseous or volatile liquids, recent studies have centered around the development of methods for mixing and analyzing less volatile liquids such as acetaldehyde, formic acid and formaldehyde. Figure 1 shows a saturator apparatus that we have developed to accomplish this task.

Previous testing had been completed using methane, ethane, and ethylene as the primary fuel stream impurity and later extended to include acetaldehyde. Testing has been established as a series of 100-hour test runs using up to 5% of the contaminant in the fuel stream with the cell construction as defined in Table 1.

FIGURE 1. Gas Mixing Set-Up for Liquid Hydrocarbons

TABLE 1. Test Cell Definition

Parameter	Value (Early)	Value (Recent)
Membrane	Nafion® 212	Nafion® 212
Anode Loading	0.4 mg/cm ²	0.4 mg/cm ²
Anode Type	50% Pt on C	50% Pt on C
Cathode Loading	0.2 mg/cm ²	0.2 mg/cm ²
Cathode Type	50% Pt on C	50% Pt on C
MEA OEM	Ion Power	Ion Power
Cell Area	25 cm ²	25 cm ²
OEM	Fuel Cell Technologies	Fuel Cell Technologies

OEM - original equipment manufacturer

Testing was conducted at 200, 600 and 800 mA/cm² with standard test conditions defined below in Table 2. Conditions were modified as defined to achieve better performance stability during testing.

TABLE 2. Definition of Major Test Parameters

Parameter	Value (Early)	Value (Recent)
Anode Temperature	80°C	80°C
Cathode Temperature	80°C	73°C
Cell Temperature	80°C	80°C
Anode Humidity	100%	100%
Cathode Humidity	100%	75%
Anode Stoich	1.3	2.0
Cathode Stoich	2.0	2.0
Anode Flow	Commensurate with Current Density	
Cathode Flow	Commensurate with Current Density	
Anode Pressure	25 psig	25 psig
Cathode Pressure	25 psig	25 psig

Acetaldehyde

Testing of the effect of acetaldehyde (CH₃CHO) on cell performance was investigated at two impurity concentrations, 100 ppm and 30 ppm. No significant effect on cell performance was found during these impurity tests.

Formic Acid

The effect of formic acid (HCOOH) on fuel cell performance was investigated at two impurity concentrations, 100 ppm and 50 ppm. Testing showed moderate degradation of the cell performance during the 100-hour durability test shown in Figure 2.

Cyclic voltammetry (CV) scans performed at a rate of 20 mV/sec before and after the impurity test show that the electrochemical area of the cathode decreased, signifying that HCOOH has a negative effect on the cathode catalyst layer. Similar scans were also performed periodically (every 20 hours – Figure 3) during contamination and recovery period to provide more details of the mechanism for contamination on the cathode. In the CV scans, the cell temperature, the dew points, and the pressures remained unchanged. Pure nitrogen was fed to the cathode at 250 sccm, while HCOOH/H₂ was fed to the anode at 250 sccm. The CV scans indicate a decrease in H₂ adsorption peaks and an oxidation peak at 0.6 V which could be caused by the presence of adsorbents on Pt surface.

100 Hour Durability Test @ 800 mA/cm²

FIGURE 2. Durability Test using 100 ppm Formic Acid

CO Corrected CV Scans during Contamination (Last Cycle Recorded)

FIGURE 3. Progressive CV Scans on the Cell

An example of an individual CV scan is shown in Figure 4. Each scan consists of four cycles. In the first CV cycle, the hydrogen adsorption peak nearly disappeared. The Pt surface appears rather than seems to be covered by adsorbents (evident by peaks at 0.4 V and 0.6 V that are not seen with pure H₂). The adsorbents are oxidized around 0.4 V and 0.6 V (e.g. CO) in the 1st cycle. In the next three cycles, recovery of H₂ adsorption peak is observed, but evidence of surface coverage still exists.

CO Corrected CV during Recovery (Last Cycle) **FIGURE 4.** CV Scans Showing Recovery

Testing to date is summarized in the matrix shown in Table 3. Testing has indicated little effect of simple hydrocarbon species on fuel cell performance; however, more complex species do appear rather than seem to affect performance.

Cationic Contaminants - The effects of cationic impurities on membrane properties have been investigated. In this regard, fully hydrated Nafion® membrane samples have been doped with concentrations of various metal cations, including Li, Na, K, Cs, Ca, Mg, Ni, Fe, Al, Cu, and Cr in an effort to study the effects of contaminant mass and valence on critical membrane properties. Studies have focused on a balance between constituents that would normally be present in the materials of construction of the fuel cell, those that might be ingested in the fuel cell from hydrogen, and those that would provide important information for contaminant modeling activities.

Membrane physio-chemical properties, including permeability of common gases such as nitrogen, hydrogen, and oxygen have been measured at very low ionic loadings.

This year we initiated collaboration with Oak Ridge National Laboratory to gain further insight into the characterization of MEAs of PEM fuel cells. The emphasis was placed on fine tuning analytical procedures and sample preparation for MEAs. We continued this work at UConn's Institute for Materials Science in preparing samples and conducting elemental mapping analysis on cation-doped MEAs to identify the ion distribution within the MEAs. These Nafion® membrane samples had been exchanged with cations in an aqueous bath having concentrations of cations ranging from 1 M to about 0.00001 M. Samples were analyzed by taking an energy dispersive X-ray spectrum of the sample in the scanning electron microscope (JEOL JSM 6335F). Some elemental mapping was done to confirm the constituents of the membrane.

Impurity Model Development – We have developed a multi-dimensional model predicting the effects of cationic contaminants on PEM fuel cells. The model is based on a previously developed multi-physics PEM fuel cell model that solves for electrochemistry coupled transport phenomena, namely mass, momentum, species, energy and charge conservation. The first step of cationic contamination implementation is the development of the submodel for the cation transport across the polymer electrolyte. To make the model as generic as possible, a multi-component cationic transport model for polymer electrolyte is developed and validated against Sodaye's (2008) experimental data. The transport model is based on the Nernst-Planck equation and combines the migration and diffusive transport of charged ions across the polymer electrolyte. The multi-component model results in $n+1$ coupled equations (n is the number of cationic impurity) solved simultaneously, as opposed to decoupled equations that can be solved separately in dilute approximation. As seen from

TABLE 3. Summary of Fuel Cell Testing Using Organic Impurities

Cell #	Impurity	Curent Density	RH (A/C)	Cell Temp	Flow Rates A/C	Description
1	100 ppm CH ₄	200 mA/cm ²	100%/100%	80°C	58.5/214 sccm	No significant degradation
2	100 ppm CH ₄	600 mA/cm ²	100%/100%	80°C	175/642 sccm	No significant degradation
3	5% CH ₄ or 5% N ₂	600 mA/cm ²	100%/100%	80°C	175/642 sccm	No significant degradation
4	100 ppm CH ₄	1800 mA/cm ²	100%/100%	80°C	234/857 sccm	No significant degradation
6	5% C ₂ H ₆	600 mA/cm ²	100%/100%	80°C	175/642 sccm	No significant degradation
7	5% C ₂ H ₄	800 mA/cm ²	100%/100%	80°C	234/857 sccm	No significant degradation
11	30 ppm CH ₃ CHO	800 mA/cm ²	100%/100%	80°C	181/664 sccm	No significant degradation
31	30 ppm CH ₃ CHO	800 mA/cm ²	100%/75%	80°C	181/664 sccm	No significant degradation
35	100 ppm HCOOH	800 mA/cm ²	100%/75%	80°C	181/664 sccm	Significant degradation

RH - relative humidity

FIGURE 5. Competitive absorption of sodium (Na⁺) and cesium (Cs⁺) ions into a Nafion® 117 electrolyte: (a) Relative occupancy when the membrane is equilibrated in a solution of NaCl and CsCl having a ratio of 1:1; (b) Relative occupancy when the membrane is equilibrated in a solution of NaCl and CsCl having a ratio of 5:1. The symbols represent Sodaye's (2008) experimental data, the solid lines represent our model predictions, the dashed lines represent Sodaye's (2008) model predictions.

Figure 5, the multi-component transport model is able to better capture the competitive exchange of proton sites with cationic species. As seen, the Na⁺ ions are faster to diffuse into membrane, so initially Na⁺ concentration is higher, however due to their higher selectivity, Cs⁺ ions are able to displace the Na⁺ ions in addition to H⁺ ions.

This submodel is incorporated into the above described multi-physics PEM fuel cell model. The effects of cation contamination are included into the properties of the polymer electrolyte, and it is currently assumed that cationic impurities neither affect the electrochemical kinetics of fuel cell reactions, nor adsorb on the catalyst surface. Figure 6 shows the concentration of Na⁺ ions in the membrane electrode assembly, where NaCl is introduced into the cathode of a PEM fuel cell. As seen, the migration and diffusion are counter-acting (i.e. migration is from anode to cathode, diffusion is from cathode to anode) therefore the cationic impurity (i.e. Na⁺) is not able to penetrate into the membrane, but

rather concentrates in the cathode catalyst layer. As a result of the Na⁺ contamination, the average current density at a cell voltage of 0.7 V and 50% relative humidity at the inlet of both anode and cathode drops from 0.42 A/cm² to 0.29 A/cm².

The model is currently being updated and improved to incorporate the effects of cationic impurities that can be introduced from anode (e.g. NH₄⁺), the potential effect of cationic impurities on the electrochemical reactions, as well as the effect on mechanical properties, and mechanical stress distributions in polymer electrolytes of operating polymer electrolyte fuel cells, based on the data we have generated previously.

Conclusions and Future Directions

Conclusions

- Simple hydrocarbons including methane, ethane, ethylene and acetaldehyde do not significantly affect fuel cell performance.
- Formic acid impurities do show an appreciable effect on performance possibly due to adsorption on the electrode surface as well as the formation of reaction byproducts such as CO.
- A multi-component cationic transport model has been created and validated against experimental data.

Future Directions

- Comprehensive evaluation of formic acid and formaldehyde to support International Organization for Standardization standard development:

FIGURE 6. Fraction of Na⁺ across the MEA

- Continued testing using standard test protocols, MEAs.
- Target low catalyst loadings (reduction from 0.4 mg/cm² to 0.1 mg/cm²).
- Develop an understanding of mechanism for performance impact.
- Modeling of effects/sharing of data.
- Extension to simple halogenated compounds.
- Continued study of effects of cations on membrane properties:
 - Application-relevant contamination types/levels.
 - Commercially relevant membranes.
 - Modeling of effects/sharing of data.
- 3. “Evaluation of the Effects of Impurities on Fuel Cell Performance and Integrity”, NRC – Canada, February, 2009.
- 4. M.F. Serincan, U. Pasaogullari, T. Molter “Effect of cathode side cationic contamination on the performance of an operating PEFC” to appear in *Proceedings of 7th ASME International Fuel Cell Science, Engineering & Technology Conference*, 8–10 June, 2009 Newport Beach, CA.
- 5. X. Zhang, U. Pasaogullari, T. Molter, J. Preston, “Influence of Ammonia on Membrane-Electrode Assemblies in Polymer Electrolyte Fuel Cells” to appear in *Proceedings of 7th ASME International Fuel Cell Science, Engineering & Technology Conference*, 8–10 June, 2009 Newport Beach, CA.
- 6. M.F. Serincan, “Multiphysics Modeling of Fuel Cells”, Ph.D. Defense, June, 2009.

FY 2009 Publications/Presentations

1. “Effects of Impurities on Fuel Cell Performance and Durability”, Modeling Workshop, Denver, CO, November, 2008.
2. “Fuel Cells and Transportation”, School of Engineering Seminar Series, The University of Vermont, December, 2008.

V.D.1 Lead Research and Development Activity for DOE's High Temperature, Low Relative Humidity Membrane Program

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Contract Number: DE-FG36-06GO16028

Subcontractors:

- BekkTech LLC, Loveland, CO
- Scribner Associates, Inc., Southern Pines, NC

Project Start Date: April 1, 2006
Project End Date: August 31, 2009

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section (3.4) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) Durability
- (C) Performance

Technical Targets

FSEC has been developing and evaluating new polymeric electrolyte PTA composite membranes to increase conductivity. FSEC is also developing standardized experimental methodologies to:

- (1) measure conductivity (in-plane and through-plane);
- (2) characterize mechanical, mass transport, and surface properties of the membranes; and
- (3) predict durability of the membranes and their membrane electrode assemblies.

The primary goal was for the membranes to meet the following DOE targets:

- A non-Nafion® membrane with a demonstrated conductivity of 0.07 S/cm at 80% RH at room temperature by the third quarter of year two.
- A membrane with a demonstrated conductivity of >0.1 S/cm at 120°C and 1.5 kPa water vapor partial pressure (50% RH measured at room temperature). This is a Go/No-Go decision point for the third quarter of year three.

Objectives

- Demonstrate conductivity of 0.07 S/cm, at 30% relative humidity (RH), 25°C using new polymeric electrolyte phosphotungstic acid (PTA) membranes.
- Demonstrate conductivity of >0.1 S/cm at 120°C and 1.5 kPa inlet water vapor partial pressure to the fuel cell stack.
- Standardize methodologies for in-plane and through-plane conductivity measurements.
- Provide High Temperature Membrane Working Group (HTMWG) members with standardized tests and methodologies.
- Organize HTMWG biannual meetings:
<http://www1.eere.energy.gov/hydrogenandfuelcells/htmwg.html>

Accomplishments

- Demonstrated conductivity of >0.07 S/cm at 80% RH at 30°C for the FSEC-3 membrane (exceeded Year 2 third quarter milestone).
- Achieved conductivity of 0.08 S/cm at 120°C and 1.5 kPa water vapor partial pressure (0.02 S/cm below Go/No-Go decision point milestone).
- Provided in-plane conductivity measurements for ten HTMWG teams and developed through-plane conductivity measurement method.
- Developed protocol for standardized testing of performance.
- Verified protocol in-house and distributed to HTMWG members at the May 2009 HTMWG meeting.

Introduction

Proton exchange membrane fuel cells (PEMFCs) have increasingly received worldwide attention due to their potential use in the hydrogen economy. Generally, two regimes of PEMFC operation exist: the typical operating temperatures between 60-80°C, and elevated temperatures higher than 100°C. The ability for current automotive radiators to reject heat is insufficient at continuous full power waste heat loads for 60-80°C fuel cell stack temperatures. Running the stack at 120°C under full load would allow the use of radiators similar to those available in automobiles today. This has driven the need for development of high-temperature membranes and membrane electrode assemblies that could operate at temperatures of up to 120°C, low RH and near atmospheric pressure.

The objective of the current project is to develop a fuel cell membrane material that meets the goals outlined by the DOE in the multi-year plan. Additional goals are: operation at elevated temperatures (up to 120°C), with a demonstrated conductivity of >0.1 S/cm at 120°C and 1.5 kPa inlet water vapor partial pressure to the fuel cell stack (50% RH measured at room temperature). The material needs to operate over a range of operating conditions from -20 to 120°C because conductivity at the lower temperature is necessary to achieve both quick start-up from cold temperatures and efficiency targets. Inlet water pressures of 25 kPa today are acceptable, but 1.5 kPa at the end of this five-year project is required. The membrane electrode assemblies (MEAs) fabricated from the membranes must meet durability targets in the aggressive environment of a fuel cell; i.e., the material must have good chemical stability and be resistant to oxidation by radicals produced in the cell during operation.

Approach

FSEC is a development leader, as well as a membrane developer. As development leader, FSEC develops and provides protocols, conducts standardized tests on samples from the group members, and provides fuel cell training with yearly hands-on “Short Courses” on conductivity and fuel cell performance testing. As a membrane developer, FSEC was developing membranes based on poly[perfluorosulfonic acids] (PFSAs) and on sulfonated poly(ether ether ketone)s and sulfonated poly(ether ketone ketone) (SPEEK/SPEKK). New composite membranes containing small particle stabilized phosphotungstic acid were fabricated using non-Nafion®-based PFSAs of equivalent weight (EW) lower than 1100, SPEEKs with various sulfonation degrees, or SPEKK as the proton-conducting component in a blend with either poly(ether sulfone) or SPEKK

with different sulfonation levels. The FSEC team, along with subcontractors BakkTech, LLC, and Scribner Associates, working with the fuel cell community, are developing standardized experimental methodologies to: (1) measure conductivity as a function of RH and mechanical properties of membranes; (2) characterize mechanical, mass transport and surface properties of the membranes; and (3) predict durability of the membranes and their membrane electrode assemblies, which have been fabricated by the FSEC team for the in-house research program and that will be fabricated for membranes provided by the HTMWG. FSEC will develop and provide the DOE’s HTMWG with standardized tests and methodologies, along with short course education offerings on these test methodologies and membrane electrode assembly fabrication techniques so that all research program members will be able to understand and reproduce these processes in their own facility. An easily implemented protocol and rapid test apparatus for evaluating the through-thickness conductivity (or resistance) of membranes over a broad range of conditions has also been developed.

Results

The Go/No-Go milestone occurred late in this contract year. To support the effort for the HTMWG members, conductivity measurements were made on membranes supplied by Fuel Cell Energy, Case Western Reserve University, University of Tennessee, Vanderbilt University, Virginia Polytechnic Institute and State University, Penn State University, Colorado School of Mines, Clemson University, and Giner, Inc. The results of these tests can be seen in Figure 1.

Over the first three years of the project, FSEC has evaluated five composite membranes: FSEC-1, FSEC-2, FSEC-3, FSEC-4, and FSEC-SLR. The first four membranes are poly[perfluorosulfonic acid]-phosphotungstic acid composite membranes, while the FSEC-SLR is a SPEEK-phosphotungstic acid

FIGURE 1. Conductivity of Funded Project Membranes

composite membrane. The FSEC-1 membrane is a 25-30 μm thick composite membrane, prepared using a solution of an 1100 EW ionomer and PTA, cast on a thin, porous Teflon[®] support. The FSEC-1 membrane has been shown to be more durable than Nafion[®]-like membranes because of the support material, the presence of heteropolyacids, which decompose free radical oxidizing agents formed during fuel cell operation, and a higher temperature fabrication process that improves durability. The FSEC-2 membrane uses a 950 EW ionomer in place of the 1100 EW ionomer, and the FSEC-3 membrane uses a 750 EW ionomer. While the manufacturing processing steps are the same in the fabrication of FSEC-1, -2, and -3, the process conditions for the manufacture of FSEC-1 have been optimized to obtain maximum conductivity and durability. Since the conductivity of early FSEC-3 membranes showed substantial improvements over both the FSEC-1 and -2 membranes, FSEC-2 was not optimized. While some optimization process development of FSEC-3 has been completed, the lower EW PFSA ionomer has proven to be more sensitive to changes in the process variables than the higher EW ionomer. The improvements in conductivity that occurred as a result of the changes to the process can be seen in Figure 2. Manufacturing process changes, including the use of high-boiling solvents, modified drying times, stabilization with cesium, and adjusted heat-treat conditions for the 750 EW ionomer/PTA composite membrane, have shown conductivities (measured at FSEC) between 75 and 80 mS/cm, and are shown as FSEC-4 in Figure 2.

While significant conductivity improvements over Nafion[®] were achieved in the FSEC series of membranes, the Go/No-Go milestone was not achieved. As a result, the membrane development under this project has been halted.

The official conductivity measurements that were made under this project were made using the in-plane method. However, conductivity in an operating fuel cell is through-plane. As a result, a new novel method for making through-plane measurements was developed. A

FIGURE 2. Conductivity of FSEC Membranes

FIGURE 3. Comparison of In-Plane and Through-Plane Conductivity of Nafion[®] NRE-212

comparison of the two methods was made by measuring the conductivity of a number of standard Nafion[®] membranes. As can be seen in Figure 3 for Nafion[®] NRE-212, the conductivities were very similar for the two methods.

The DOE goal of this project is to meet the conductivity target at 120°C and 50% RH, but additional targets must also be met; for example, chemical and mechanical stability, cycle life of over wide ranges of operating temperature, minimal gas crossover, cost, tolerance to condensed water, and ability to be started from -40°C are also important. Meeting all of these membrane targets, as well as MEA targets, will ultimately be required to achieve the DOE-outlined 2015 goals. In preparation for the next two years of the project, FSEC has developed a standard protocol for performance testing of MEAs that will be constructed from membranes supplied by the HTMWG members remaining after the Go/No-Go milestone. FSEC has verified this protocol using commercial MEAs, as well as MEAs with FSEC series membranes. This protocol was distributed to the working group at the meeting in May 2009. An additional protocol has been written for accelerated endurance testing and is being verified.

Conclusions and Future Directions

- Significant progress has been made in improving the conductivity and performance of membranes.
- In accordance with the DOE decisions after the Go/No-Go Review, membrane development under this project has been halted.
- Verification of the accelerated endurance test protocol will be completed.
- Membrane electrode assemblies will be prepared from team member membranes.
- Performance testing of MEAs will be conducted.

FY 2009 Publications/Presentations

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2. Rodgers, M. P.; Agarwal, R.; Pearman, B.; Li, B.; Slattery, D.; Choi, P.; Mohajeri, N.; Bonville, L.; Kunz, H. R.; Fenton, J. M. **Accelerated durability testing of perfluorosulfonic acid MEAs for PEMFCs.** ECS Transactions (2008), 16(2), 1951-1959.
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7. Cooper, K, **Advances in Polymer Electrolyte Membrane Fuel Cell Systems 2009,** Asilomar Conference, Pacific Grove, CA, February 15–18, 2009.

V.D.2 Dimensionally Stable High Performance Membrane

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Contract Number: Grant DE-FG36-06GO16035

Subcontractor:

State University of New York
Environmental Science Forestry (SUNY-ESF)
Syracuse, NY

Project Start Date: April 3, 2006

Project End Date: April 1, 2011

Objectives

- Determine the effect of pore size and substrate thickness on conductivity and water uptake.
- Demonstrate polymerization conditions suitable for bulk polymerization of perfluorinated sulfonic acids (PFSA's).
- Demonstrate, by the 3rd Quarter 2007, membrane conductivity of 0.07 S/cm, at 80% relative humidity (RH), at room temperature, and using non-Nafion[®] materials. Samples will be prepared and delivered to the Topic 2 Awardee.
- Go/No-Go Decision: Demonstrate, by the 3rd Quarter 2008, membrane conductivity >0.1 S/cm, at 25% RH at 120°C, using non-Nafion[®] materials. Samples will be prepared and delivered to the Topic 2 Awardee.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program

Multi-Year Research, Development and Demonstration Plan:

- (A) Durability
- (B) Cost
- (C) Performance

Technical Targets

Progress has been made in achieving the DOE 2010 Hydrogen, Fuel Cells and Infrastructure Technologies Multi-Year Research, Development and Demonstration Plan targets. Table 1 lists the DOE's technical targets and where our research stands to date. There are two other DOE targets for membranes relating to durability, which we have not yet addressed.

TABLE 1. DOE Technical Targets and GES Status

Characteristic	Unit	2010 Target	GES DSM Status
Inlet water vapor partial pressure	kPa	1.5	20 ^a
Oxygen cross-over	mA/cm ²	2	1.5 ^b
Hydrogen cross-over	mA/cm ²	2	1.8 ^b
Membrane Conductivity	S/cm		
Operating Temperature			
95°C		0.10	0.093 ^a
20°C		0.07	0.083
-20°C		0.01	Not tested
Operating temperature	°C	≤120°C	95°C
Area resistance	Ohm*cm ²	0.02	0.03 ^c
Cost	\$/m ²	20	~100
Durability with cycling <80°C		5,000 hours	10,000 cycles
Unassisted start from low temperature	°C	-40	Untested
Thermal cyclability in presence of condensed water		Yes	Yes

^a95°C with H₂/air at 20 psia balanced pressure. H₂/air stoichiometry of 1.1/2.0

^bCross-over measured for 1 atm of pure H₂ and pure O₂ at 95°C and 50% RH.

^cFor 18 μm two-dimensional laser-drilled material operating at conditions listed above in (^a)

Accomplishments

- Successfully demonstrated that dimensionally stable membranes (DSMs) based on laser drilling pores restrain x-y swelling (<5%) with a wide range of pore size and thickness and substrate materials.

- Effective methods of generating new PFSA polymers have been generated. These have been generated via bulk polymerizations which will allow for the direct formation of the composite membrane.
- Short-term (DOE 2008 High Temperature Membrane) conductivity targets have been met for room temperature conductivity, promising results confirmed by independent lab (Bekktech) using a two-dimensional laser-drilled (2DSM) support material, resulting in passing the go/no-go decision point and continuation of the project:
 - 0.0852 S/cm at 30°C and 80% RH vs. goal of 0.07.
 - 0.031 S/cm at 25% RH and 120°C is below DOE target, but getting closer.
 - 0.093 S/cm achieved at 120°C and 50% RH close to DOE upper target for RH.
- New PFSA material generated at SUNY-ESF and incorporated in three-dimensional support material (3DSM):
 - Demonstrates 0.08 S/cm conductivity at 30% RH, approaching DOE ultimate target of 0.10 S/cm at 25% RH.
 - DOE Conductivity Targets met with 3DSM and homopolymer; GES results significantly higher than Bekktech.
- Demonstrated improved fuel cell performance at 95°C and 25% RH, 7 psig H₂/air (0.68 V at 500 mA/cm²).
- Both commercially available polyethersulfone (PES) and ultra-high molecular weight polyethylene (UPE) successfully incorporated as porous supports in 3DSM:
 - Swelling reduction similar to 2DSM.
 - Conductivity penalty of support ~33%.
- Increased mechanical durability with 2DSM and 3DSM, demonstrated through RH cycling (10,000 cycles, 2 min bone-dry, 2 min 95°C dew point).
- Collaborating with Millipore for thinner 3DSM support samples.

Introduction

PFSA materials have demonstrated promising high temperature/low RH conductivity, yet are still unsuitable for automotive applications. Increasing acid content and making the membranes thinner are two methods for lowering the resistance of these materials. However, each of these methods has a negative impact on mechanical durability of the membrane. GES is trying to combine the good conductivity properties of high acid

content PFSAs and improve their mechanical properties by making composite materials.

Approach

GES's approach is to use very high acid content PFSA materials and support them with high-strength non-acidic materials. This involves generating the PFSA polymers which is being done with our partners at SUNY-ESF, generating the supports, and finally forming and characterizing the composites.

Results

GES has successfully imbedded high acid content PFSA materials in laser-drilled supports consisting of either polysulfone or polyimide (Kapton). Figure 1 shows the laser-drilled support, as well as the composite, DSM. A matrix of support material, pore size, support thickness and equivalent weight (EW) of PFSA fill has been completed. When the supports are 10% of the total material and have no greater than 60% void space, they nearly eliminate swelling in the x-y direction. This is true regardless of hole size, acid content of the PFSA fill material, or whether polysulfone or polyimide was used as the support. Fuel cell testing has been carried out on a 2 mil DSM consisting of a 1/3 mil polyimide support filled with 700 EW PFSA and the 2DSM far outperforms Nafion® 112 performance.

A sample composite material with low EW PFSA and 10% support material has demonstrated 2-3x the conductivity of Nafion® 112, the PFSA standard, over the entire range of RH as shown in Figure 2. This conductivity still falls short of the DOE target however, as seen in the figure. Previously it appeared that this approach would not be able to reach the DOE's cost target, however in a separate DOE contract GES has demonstrated a successful method of micro-molding these substrates.

Commercially available porous supports offered an alternative to the cost-prohibitive 2DSM supports: an unforeseen development from the original proposal but very promising as the 3DSMs demonstrated

FIGURE 1. Scanning electron microscope images of laser-drilled DSM support (left) and support filled with PFSA (right).

FIGURE 2. Conductivity of 2DSM membrane consisting of 700 EW PFSA in a polyimide support as well as two 3DSMs: one with the SUNY-ESF homopolymer at 80°C and a second with highly cross-linked PSEPVE. Insets of the 2DSM and 3DSM membranes are shown.

the dimensional stability and improved mechanical properties of the 2DSM. We successfully incorporated 1100 EW PFSA ionomers into commercially available PES and unsaturated polyester (UPE) and tested the membranes under electrolysis conditions, as seen in Figure 3. Electrolyzer testing was used as the membranes were too thick for fuel cell testing. Electrolyzer testing allows us to test the membranes in an electrochemical cell and determine the performance penalty due to the support, even with a thick membrane. As seen in the figure, a 4 mil PES membrane behaves similarly to a 5 mil unsupported membrane, showing that the conductivity penalty due to the support is slightly greater than 25%. The thinnest PES porous support commercially available is 4 mils thick. We are currently working with Millipore on thinner supports so that we can conduct fuel cell testing on the 3DSMs. They have supplied us with 1 and 2 mil thick UPE and have successfully incorporated low EW PFSA ionomers into the thinner supports and tested through plane conductivity, shown in Table 2. As seen in the table we are now able to generate very thin membranes without a large conductivity penalty. For example the 0.7 μm

UPE membrane has a final thickness of 0.4 mils with only a 20% conductivity penalty compared to neat 1100 EW PFSA. Unfortunately, we have not been as successful in incorporating the lower weight PFSA materials into this support, which will be an area of concentration in the upcoming year.

To further increase conductivity, PFSA's with even higher acid content are being synthesized at SUNY-ESF under the direction of Israel Cabasso. A large number of materials have been synthesized, including the homopolymer of just the active monomer. Improvements in the synthesis of this polymer have led to a film-forming ionomer that can be readily incorporated in GES's 3DSM structures. In the previous year we demonstrated that this material has a conductivity that is approximately twice that of the best 2DSM material to date and approximately five times that of Nafion® 112 over an

entire range of RH as seen in Figure 2. Also seen in the figure is that this material comes very close to meeting

FIGURE 3. Electrolyzer performance of a 4 mil thick PES 3DSM and a 2 mil thick UPE 3DSM membrane with 1100 EW.

TABLE 2. Through-Plane Conductivities of Differently Prepared Samples

Material/Pore Size	Ionomer	Starting Thickness (mils)	Final Thickness (mils)	Through-Plane Conductivity (S/cm)
Nafion® 111	1100 EW	1	1	0.05
0.45 μm UPE	1100 EW	2	2.1	0.023
0.7 μm UPE	1100 EW	1	0.4	0.040
0.7 μm UPE	850 EW	1	1.5	0.045
0.7 μm UPE	700 EW	1	0.6	0.018

the DOE target for conductivity down to 25% RH. Unfortunately this material swelled excessively in water.

Work at SUNY in this past year has centered on reducing this swelling while maintaining the high conductivity at low RH. A highly cross-linked perfluoro (4-methyl-3,6-dioxaoct-7-ene) sulfonyl fluoride (PSEPVE)-based polymer was cast and characterized for conductivity at Giner Electrochemical Systems. The conductivity of this polymer was quite high at low levels of RH as seen in Figure 2. Surprisingly the conductivity at higher levels of RH does not increase as quickly as the non-crosslinked materials. We believe that this is due to the lower water contents at higher RH due to the cross-linking. Water sorption isotherms of this material will be conducted to confirm this conclusion.

Conclusions and Future Directions

The DSM with laser-drilled supports successfully has been shown to restrain x-y swelling in high acid content PFSA's over a range of composite dimensions and compositions. Though 2-3 times more conductive than Nafion® 112, it still is short of the DOE's conductivity targets. Work has been done to synthesize PFSA's with even higher-acid content, including the homopolymer that contains only the functional monomer. This polymer, when incorporated in the 3DSM has come very close to meeting the DOE targets. This polymer is water soluble however, and eventually leaches out of the 3DSM support. Efforts have begun to cross-link this polymer to make it insoluble and resulted

in a polymer with similar low RH performance that is hydrolytically stable. RH cycling of the 2DSM and 3DSM materials has been completed to demonstrate these materials superior mechanical attributes; each of them surpassing 10,000 cycles. We are currently focusing on preparing thin 3DSMs with low EW ionomer for fuel cell testing. Millipore is assisting in this effort.

Special Recognitions & Awards/Patents Issued

1. 2009 DOE Hydrogen Program Review R&D Award.

FY 2009 Publications/Presentations

1. Mittelsteadt, C.M., VanBlarcom, S. Liu, H., Wie, X., Johnson, F., Cabasso, I. "Dimensionally Stable Membranes" Presentation at FreedomCar, Michigan, April 2009.
2. Mittelsteadt, C.M., VanBlarcom, S. Liu, H., Wie, X., Johnson, F., Cabasso, I. "Dimensionally Stable Membranes" Presentation at Washington, D.C. Semi-annual review Jun 2008.
3. Liu, H., M. Chen, J. Willey, C. Mittelsteadt, A. LaConti, "High Performance, Dimensionally Stable Membrane" 2008 Fuel Cell Seminar & Exposition, Phoenix, Arizona, Oct. 27-30, 2008.
4. Liu, H. "Performance and Durability of Dimensionally Stable Membrane" Fuel Cells Durability & Performance 4th Annual International Conference, Las Vegas, NV, Dec. 11-12, 2008.

V.D.3 New Proton Conductive Composite Materials with Co-Continuous Phases Using Functionalized and Crosslinkable VDF/CTFE Fluoropolymers

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Project End Date: April 30, 2009

Objectives

- Synthesize new cross-linkable polyolefin-based proton conductors with excellent mechanical strength and thermo and chemical stability.
- Synthesize highly conductive inorganic of different structural types with different functional groups for use in composite membrane preparation.
- Test the inorganic in Nafion[®]-based composite membranes to select the most promising materials for the future composite membranes based on the newly developed polymeric materials.
- Develop a new membrane material based on the combination of inorganic proton conductors with a newly developed polyolefin based proton conductors to be used in proton exchange membrane (PEM) fuel cell at 120°C and 25-50% relative humidity (RH).

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section (3.4.4) of the Hydrogen, Fuel Cells and Infrastructure Technologies

Program Multi-Year Research, Development and Demonstration Plan:

- (A) Durability
- (B) Cost
- (C) Performance
- (E) System Thermal and Water Management
- (F) Air Management

Technical Targets

This project is conducting fundamental studies on polymer/inorganic composite membranes. Insights gained from these studies will be applied toward the design and synthesis of composite membranes that meet the following DOE 2010 targets for membranes (automotive):

- Membrane conductivity at 120°C and 1.5 kPa water pressure 0.1 S/cm.
- Durability: 5,000 hours.
- Cost: \$5/kWh.

Accomplishments

- Synthesized new cross-linkable polyolefin-based proton conductors with excellent mechanical strength, which are very stable under free radical conditions.
- Synthesized highly conductive inorganic of different structural types with different functional groups such as cylindrical mesoporous silica (SBA-15), mesoporous silica with arrays of hexagonal channels (MCM-41), S-ZrO₂, sulfonic acid functionalized cubic cage mesoporous silica (HOM-1), and P/Si gels for use in composite membrane preparation.
- Characterized inorganic materials by powder X-ray diffraction, scanning electron microscopy (SEM), Brunauer-Emmett-Teller (BET) surface area, porosity, ion exchange capacity (IEC), and conductivity.
- Achieved a conductivity of 10 mS/cm for S-ZrO₂ at 120°C and 100% RH and 100 mS/cm for phosphosilicate gel with P/Si ratio of 1.5 at 120°C and 70% RH.
- Tested functional inorganic in Nafion[®]-based composite membranes; conducted comparative measurements of swelling, IEC and conductivity of Nafion[®]/inorganic composite membrane with different type of inorganic, different inorganic loading and different fabrication techniques.

- Tested the effect of inorganic on the composite membrane performance in a fuel cell.

Introduction

This project addresses one of the main challenges in present-day PEM fuel cell technology: to design a membrane capable of maintaining high conductivity and mechanical integrity when temperature is elevated and water vapor pressure is severely reduced. If this goal is reached, the fuel cell operating pressure can be kept low, which would make the PEM fuel cell much more cost efficient and adaptable to practical operating conditions and facilitate its faster commercialization particularly in automotive and stationary applications.

Approach

Our approach addresses the barriers in the development of PEMs such as high-temperature low-RH conductivity and durability and DOE conductivity milestone of 100 mS/cm at 120°C, 50% RH. To overcome this barrier, the approach being employed to develop a composite membrane with hydrophilic proton-conductive inorganic material and the proton conductive polymeric matrix that is able to “bridge” the conduction paths in membrane. The unique aspect of our approach is the use of highly functionalized inorganic additives to benefit from their water retention properties and high conductivity as well.

Results

In the past year, the main effort was centered on the development of a new class of proton conducting materials, synthesis and characterization of highly conductive inorganic and testing the inorganic in composite membranes. Novel cross-linked polyolefin copolymers that contain both crystalline hydrophobic phase and amorphous hydrophilic phase with co-continuous and clear phase separated morphology was synthesized. The major reason of changing the polymer to polyolefin is to improve the chemical and mechanical stability of PEM composites. Polyolefins, such as polyethylene (PE) and polypropylene (PP), are known to be very stable in strong acids and bases, as well as under free radical conditions. Both PE and PP are also semicrystalline thermoplastics with excellent mechanical strength, as well as most hydrophobic materials. This combination could provide a stable polymer matrix with limited swelling and the ability to retain water in the inorganic domains for transporting protons at 120°C. We have developed several powerful methods in the preparation of functional PE and PP polymers, which offer the potential to engineer polyolefin-based

PEM structure (concentration of sulfonic acid groups for increasing conductivity, degree of crosslinking for controlling swelling). The structure of the newly synthesized polyethylene based proton conductor (PE) is shown in Figure1.

Inorganic proton conductors of different structural types with different functional groups, such as alkane sulfonic functionalized cylindrical mesoporous silica (SBA-15), sulfonic acid functionalized mesoporous silica with arrays of hexagonal channels (MCM-41), sulfated zirconia (S-ZrO₂), sulfonic acid functionalized cubic cage mesoporous materials (HOM-1), and phosphosilicate gels with different P/Si molar ratios were synthesized. All the samples were characterized by powder X-ray diffraction and SEM. The BET surface area and porosity of pellets were measured by N₂ adsorption/desorption isotherm analysis. The IEC was measured by titration with NaOH solution after the completion of ion exchange with NaCl. The proton conductivity of the inorganic was measured using previously designed device and measurement method.

To compare the properties and behavior of different inorganic materials under fuel cell conditions, we prepared and characterized the composite membranes with these inorganic proton conductors. Nafion[®] was chosen as the reference matrix material for such series because it is the best studied polymer with well-known properties. Three different techniques were used to fabricate Nafion[®]/inorganic composite membranes by: (1) blending of inorganic powders with Nafion[®] solution followed by casting and annealing, (2) in situ forming the inorganic particles from infiltration of precursor solution into Nafion[®] film, and (3) in situ forming the inorganic particles from precursor in Nafion[®] solution followed by casting and heat treatment. Technique (1) was used for the preparation of composite membranes with all inorganic materials, while techniques (2) and (3) were used for the preparation of Nafion[®]/P-Si gel composite membranes only.

The membranes prepared by technique (1) were tested for swelling, IEC, conductivity and fuel cell performance. It was found that the IEC of all Nafion[®]/inorganic composite membranes was higher than that

FIGURE 1. New Polyethylene-Based Proton Conductor

of Nafion®. The conductivity of composite membranes with 10% of different sulfonated inorganic, was different for different membranes but not higher than the conductivity of recast Nafion®. None of these inorganic materials enhanced the conductivity of polymeric matrix. The conductivity measurements of composite membranes were in agreement with their IEC. No correlation between membrane conductivity and swelling was found. The effect of the inorganic content on the membrane conductivity was evaluated on a series of Nafion®/SiO₂-SO₃H composite membranes with SiO₂-SO₃H content of 10-120% from the amount of polymeric matrix. The increase in SiO₂-SO₃H content above 10% gradually decreased the membrane conductivity, probably, due to particle agglomeration. No conductivity enhancement was found when doping level was decreased to 3-0.5% (Nafion®/3%S-ZrO₂, Nafion®/0.5%P-Si, and Nafion®/0.5%SBA-15 membranes). It was found that the conductivity of Nafion®/phosphosilicate gel composite membranes was affected by surface area of P-Si gel powder.

FIGURE 2. Conductivity of Nafion®/10% P-Si gel composite membranes prepared using different techniques at 80°C (a) and 120°C (b) and different RH.

The effect of membrane fabrication technique was evaluated on Nafion®/10% phosphosilicate gel membranes. The performance of the membrane prepared by blending of inorganic powders with Nafion® (Technique 1) was the lowest. The performance of the membranes prepared by in situ formation of inorganic particles in Nafion® (Techniques 2 and 3) was higher and very close to each other (Figure 2). The effect of inorganic phase on membrane performance in fuel cell was much stronger. The resistance of Nafion®/10% P-Si gel composite membrane in a fuel cell was 40-50% less, and the limiting current about 40-50% higher than those of pure recast Nafion® (Figure 3).

Conclusions and Future Directions

The third year of the project resulted in the development of polyolefin-based polymeric proton conductors with excellent mechanical strength and stability under free radical conditions; intense synthesis

FIGURE 3. Performance and fuel cell resistance of Nafion®/10%P-Si gel membranes in H₂/Air fuel cell at 120°C and 50% (a) and 20% (b) RH.

and characterization of different types of functional inorganic; testing the inorganic in Nafion[®]-based composite membranes. These tests allowed us to select the most promising materials for the future composite membranes based on the newly developed polymeric materials.

The next step should be the development of composite sulfonated polyolefin/inorganic membranes. The first candidate for testing should be sulfonated PE/phosphosilica gel membrane fabricated using in situ formation Technique 3 described previously.

FY 2009 Publications/Presentations

1. Z. Zhang, E. Chalkova, M. Fedkin, C. Wang, S.N. Lvov, S. Komarneni, and T.C.M. Chung, *Synthesis and characterization of poly(vinylidene fluoride)-g-sulfonated polystyrene graft copolymers for proton exchange membrane*, *Macromolecules*, 41, (23), 9130 (2008).
2. C. Wang, E. Chalkova, C. Lute, M. Fedkin, S. Komarneni, T.C.M. Chung, and S. Lvov, *Proton conductive inorganics for composite membranes in PEM fuel cells*, *ECS Trans.*, 16 (2), 1451 (2008).
3. M. Chung, Z. Zhang, E. Chalkova, C. Wang, M. Fedkin, S. Komarneni, and S.N. Lvov, *Recent advance in proton conductive materials using styrene grafted and sulfonated VDF/CTFE fluoropolymers*, *ECS Trans.*, (2008) submitted.
4. E. Chalkova, C. Wang, S. Komarneni, J. Lee, M. Fedkin, and S. Lvov, *Composite proton conductive membranes for elevated temperature and reduced relative humidity PEMFC*, *ECS Trans.*, (2009) submitted.
5. C. Wang, E. Chalkova, C. Lute, M. Fedkin, S. Komarneni, T.C.M. Chung, and S. Lvov, *Proton conductive inorganics for composite membranes in PEM fuel cells*, 14th ECS Meeting, Hawai, October15, 2008.
6. M. Chung, Z. Zhang, E. Chalkova, C. Wang, M. Fedkin, S. Komarneni, and S. N. Lvov, *Recent advance in proton conductive materials using styrene grafted and sulfonated VDF/CTFE fluoropolymers*, 13th ECS Meeting Phoenix, May 18, 2008.
7. C. Wang, E. Chalkova, M. Fedkin, S. Komarneni, T.C.M. Chung, and Serguei N. Lvov, *Conductivity studies of inorganic proton conductors for composite membranes in PEM fuel cells*, 13th ECS Meeting Phoenix, May 18, 2008.

V.D.4 Poly(cyclohexadiene)-Base Polymer Electrolyte Membranes for Fuel Cell Applications

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Contract Number: DE-FG36-06GO16037

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Start Date: April 1, 2006

Project End Date: September 30, 2009

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) Durability
- (B) Cost

Technical Targets

This project is targeted toward the development and characterization of PEMs that can meet conductivity requirements specified by DOE (conductivity = 0.1 S/cm at 50% RH at 120°C), as well as achieving low cost and meet the following DOE 2010 performance criteria:

- Cost: \$25/kW_e
- Durability with cycling: 5,000 hours at an operating temperature >80°C
- Survivability: -40°C
- Thermal cyclability in the presence of condensed water
- Area specific resistance: 0.02 Ohm-cm²
- Hydrogen crossover: 2 mA/cm²
- Oxygen crossover: 2 mA/cm²
- Inlet water vapor partial pressure: <1.5 kPa
- Operating temperature: ≤120°C

Objectives

- Design, synthesize and characterize new non-Nafion[®] polymer electrolyte membrane (PEM) materials that conduct protons at low (25-50%) relative humidity (RH) and at temperatures ranging from room temperature to 120°C.
- To achieve these objectives, a range of homopolymer and copolymer materials incorporating poly(cyclohexadiene) (PCHD) will be synthesized, derivatized, and characterized.
- Characterize thermal stability of these materials.
- Identify molecular relaxations that might impact mechanical properties, temperature ceiling for fuel cell operation, and water and proton transport and durability using dynamic mechanical and dielectric relaxation techniques.
- Inorganic, membrane in situ sol-gel modifications of membranes to improve high temperature water retention and mechanical durability.

Accomplishments

- Thinner crosslinked (5 ~ 10 mol%) and sulfonated (10 ~ 45 mol%) PCHD fuel cell membranes were synthesized and characterized with elemental analysis, dynamic mechanical analysis (DMA), thermogravimetric analysis (TGA), and proton conductivity. With thinner membranes, proton conductivity has reached as high as 156 mS/cm at room temperature and 100% RH, which is much higher than that of Nafion[®] NRE-212 (~70 mS/cm).
- Three diblock copolymers of PCHD and PEG (polyethylene glycol) with different weight percent PEG (5.0%, 10%, 9.5%) were synthesized and characterized.
- New types of fuel cell membranes were prepared by sequential crosslinking and sulfonation of polymer blends or block copolymers of PCHD and PEG.
- Addition of PEG made a big jump in proton conductivity at high RH (322 mS/cm *vs.* 156 mS/cm)

and also enhanced proton conductivities at low RH. Copolymerization causes another considerable jump in conductivity so that membranes have very impressively high conductivity (410 mS/cm) at 100% RH and higher conductivity than that of Nafion® NRE-212 even at RH as low as 20%.

- The proton conductivity of the crosslinked and sulfonated PCHD-PEG block copolymer membrane XPCHD_1009_SPCHD_102 measured at BakkTech was 82.5 mS/cm at 80.3% RH at 30°C. Therefore, the Year 2 milestone of demonstrating conductivity of 70 S/cm at 80% RH at 30°C has been met. However, the final conductivity requirements specified by DOE (conductivity = 0.1 S/cm at 50% RH at 120°C) has not been met yet and is our goal of on-going effort.
- The resulting membranes are thermal stable up to 200°C and resistant to chemical degradation. Moreover, they are also very flexible and have mechanical integrity.
- The cost of membranes can be as low as \$10/m², about 1.5% that of Nafion® (about \$800/m²), making these membranes very attractive and commercially feasible for high-temperature fuel cell applications.
- Growth of inorganic nanoparticles within the hydrophilic domains of membranes is underway.

Introduction

The goal of this project is to create and develop low-cost fuel cell membranes having sufficiently high proton conductivity at high temperatures, as well as high chemical and mechanical durability. PCHD is of interest as an alternative PEM material due to its ring-like structure, which imparts superior mechanical and thermal properties, and due to the fact that PCHD can readily be incorporated into a range of homopolymer and copolymer structures. Furthermore, PCHD can be aromatized, sulfonated, or fluorinated, allowing for tuning of key performance properties such as conductivity, hydrophilicity, permeability, morphology, thermal stability, crystallinity, and cost. The basic building block, 1,3-cyclohexadiene, is a hydrocarbon monomer that could be inexpensively produced on a commercial scale (pricing typical of other hydrocarbon monomers).

To further manipulate and optimize the properties of the PCHD-based membranes, inorganic modification will be carried out through polymerization of metal alkoxides within hydrophilic regions of the membranes via sol-gel reactions. Such modification can improve mechanical and thermal properties of the membrane and also shows great promise for addressing thermal

and water management issues. Thus, these membranes are expected to meet conductivity requirements laid out in this DOE solicitation at elevated temperatures (conductivity = 0.1 S/cm at 50% RH at 120°C).

Approach

A potentially inexpensive monomer, 1,3-cyclohexadiene, can be polymerized to yield a range of novel polymers and copolymers incorporating an unsaturated six-membered ring into the polymer backbone. Mays' group is synthesizing a range of homopolymer and copolymer materials incorporating PCHD. Type 1 membranes are composed of crosslinked, sulfonated, and optionally aromatized PCHD. Type 2 membranes are block copolymers of sulfonated PCHD with poly(vinylidene fluoride), while Type 3 membranes are sulfonated and fluorinated statistical copolymers of PCHD and poly(α -methylstyrene). Since Type 2 and 3 membranes involve fluorination, it would be fairly difficult to obtain membranes of low-cost. Therefore, most of the synthesis work so far has focused on the synthesis and optimization of the Type 1 membranes. In order to reach high proton conductivity, especially at low RH, very high degree of sulfonation should be and could be reached. In general, the higher the degree of sulfonation is, the higher the proton conductivity is. However, "over-sulfonated" membranes always had too weak mechanical strength. A delicate balance between degree of sulfonation and good mechanical strength much be obtained. Therefore, it is the maintaining of good mechanical strength that limits higher extent of sulfonation. This dilemma forced us to use PEG as an additive/plasticizer or synthesize a block polymer of PCHD and PEG to increase proton conductivity instead. It turns out that the addition of PEG did make a big jump in conductivity.

The mechanical and thermal properties of these materials are characterized by DMA, TGA, and strategies for growing nanoscale metal oxide nanoparticles within the membranes (to improve proton conductivity, mechanical durability and high temperature fuel cell performance by water retention) are being developed. A working hypothesis is that relaxations, i.e., long and short range polymer motions, interact with water cluster dynamics and thereby affect proton hopping along hydrogen bonded water molecules. Molecular motions of membranes are characterized by broadband dielectric spectroscopy and correlated to proton conductivity at different temperatures. Membrane electrode assemblies (MEAs) of the membranes are prepared and checked for their performance and durability via open circuit voltage (OCV) test. Membranes degraded chemically via Fenton's reagent as well as OCV degraded ones are analyzed with broadband dielectric spectroscopy to investigate their degradation mechanisms.

Results

Most of the synthesis work to date has focused on the Type 1 membranes. These materials require the polymerization of 1,3-cyclohexadiene, followed by crosslinking of PCHD in membrane form and sulfonation of the materials. Although sulfonated crosslinked PCHD membranes such as XPCHD_1001_SPCHD_105 can obtain proton conductivity as high as 130 mS/cm at 100% RH (see our previous annual report), higher than Nafion® NRE-212 (68 mS/cm) under the same conduction, their conductivities drop so sharply with decreased humidity that the conductivities are lower than that of Nafion® NRE-212 at RH lower than 80%. Therefore, it is very critical to increase proton conductivity of our fuel cell membranes at low RH in order to meet DOE final conductivity requirement. Three different yet complementary strategies toward the conductivity goal have been taken:

- Creation of a thinner cross-linked PCHD membrane by using half amount of PCHD, followed by sulfonation.
- Creation of a cross-linked membrane from a polymer blend of PCHD and PEG, followed by sulfonation.
- Synthesis of a block polymer of PCHD and PEG, followed by sequential crosslinking and sulfonation (see Figure 1).

Characterization of Membranes

Optimization of Proton Conductivity of Crosslinked PCHD Membranes

Proton Conductivity. New membrane batches were prepared by Mays and characterized by Mauritz for conductivity, thermal and mechanical properties. Based on previous conductivity measurements, (DOE reports starting September 2007) Mays has been optimizing macromolecular chemistry for high conductivity and better sample mechanical integrity.

Proton conductivities were first measured at room temperature after soaking membranes in dionized water and then mounting them in a four point probe conductivity cell immersed in water. Before, electrical impedance measurements were performed in the frequency range 0.5 kHz to 1 MHz and samples were soaked in water for 24 h. The Z' intercept from the semicircle in Nyquist plots was taken as membrane resistance to calculate conductivity (σ).

Conductivities in Table 1 for new batch samples are higher than that of Nafion® under the same test conditions (≈ 0.07 S/cm). Some membranes have σ values up to 0.41 S/cm under these conditions. Addition of PEG is responsible for the large conductivity increase. Copolymerization gives higher values than blending PCHD with PEG and causes another considerable jump in conductivity.

FIGURE 1. Synthetic Strategy to Type 1 Membranes

TABLE 1. Effect of blending vs. copolymerization of PEG ($M_n = 2,000$ g/mol) with PCHD on the conductivity of different membranes at room temperature and soaked in dionized water before measurements.

Sample	Conductivity (S/cm)
XPCHD_902_SPCHD_108 (No PEG)	0.135
XPCHD_1005_SPCHD_104 (No PEG)	0.144
XPCHD_1005_SPCHD_105 (No PEG)	0.156
XPCHD_1007_SPCHD_101 [PEG(9.1 wt%) blended with PCHD]	0.136
XPCHD_1007_SPCHD_102 [PEG(9.1 wt%) blended with PCHD]	0.207
XPCHD_1007_SPCHD_103 [PEG(9.1 wt%) blended with PCHD]	0.256
XPCHD_1008_SPCHD_101 [PEG(16.7 wt%) blended with PCHD]	0.135
XPCHD_1008_SPCHD_102 [PEG(16.7 wt%) blended with PCHD]	0.322
XPCHD_1009_SPCHD_101 [PEG(5.3 wt%) copolymerized with PCHD]	0.410
XPCHD_1009_SPCHD_102 [PEG(5.3 wt%) copolymerized with PCHD]	0.380

Six membranes were sent to BakkTech for measurements of proton conductivity at various RHs (20 to 100%) and different temperatures (30, 80, and 120°C) and the results are in Table 2. Without PEG, the proton conductivity could be slightly higher than Nafion® NRE-212 at high RH but much lower at low RH. For example, XPCHD_902_SPCHD_105 has $\sigma = 125.77$ mS/cm at 80% RH, slightly higher than that of NRE-212 (120.75 mS/cm). However, it has only half the conductivity compared with NRE-212 (18.13 vs. 36.96 mS/cm). By blending with PEG, not only do the membranes have higher proton conductivity at 80% RH,

TABLE 2. Effect of blending vs. copolymerization of PEG ($M_n = 2,000$ g/mol) with PCHD on the conductivity at 120°C at lower (80% and 50%) RHs.

Sample	Conductivity (mS/cm) 80% RH	Conductivity (mS/cm) 50% RH
XPCHD_1003_SPCHD_102 (No PEG)	28.93	2.33
XPCHD_1001_SPCHD_105 (No PEG)	108.50	17.80
XPCHD_902_SPCHD_105 (No PEG)	125.77	18.13
Nafion® NRE-212	120.75	36.96
XPCHD_1007_SPCHD_103 [PEG(9.1 wt%) blended with PCHD]	149.00	24.10
XPCHD_1008_SPCHD_102 [PEG(16.7 wt%) blended with PCHD]	182.10	33.20
XPCHD_1009_SPCHD_102 [PEG(5.3 wt%) copolymerized with PCHD]	245.10	57.60

but also have almost as high conductivity as NRE-212, for example XPCHD_1008_SPCHD_102. Membranes made from a block copolymer of PCHD and PEG had not only higher proton conductivity at 80% RH but also higher conductivity at 50% RH than Nafion® NRE-212. XPCHD_1009_SPCHD_102 had $\sigma = 245.10$ mS/cm at 80% RH ($> 100\%$ increase compared with NRE-212) and 57.6 mS/cm at 50% RH (56% increase compared with NRE-212). As shown in Figure 2a, XPCHD_1009_SPCHD_102 showed higher conductivity at all RH ranging from 100 to 20% than NRE-212 although it showed a slightly sharper decrease of conductivity vs. RH. The higher conductivity than NRE-212 at lower (50%) RH of our membranes is significant in terms of developing inexpensive non-Nafion® high temperature low humidity operable membranes.

Conductivity measurements at 120°C and different RH for some membranes were also conducted at USM using the same protocol and instrument developed

FIGURE 2. Proton conductivity at 120°C vs. RH for different membranes measured at BakkTech (a) and at USM (b).

by BekkTech. Figure 2b showed $\sigma = 50$ mS/cm for XPCHD_1010_SPCHD_101, which was prepared by copolymerizing PCHD with PEG, confirming the conclusion that PEG copolymerization improves conductivity at 120°C and low RH. New samples have been prepared to achieve the DOE target ($\sigma > 0.1$ S/cm at 50% RH at 120°C) conductivity at 120°C but we have not yet measured their conductivities.

Water Uptake. Membrane water uptakes at different temperatures vs. RH were determined using an accurate vapor sorption analyzer (Q5000-TA Instruments). Figure 3 shows vapor pressure isotherms of PCHD (copolymer with PEG) based membranes measured at 25 and 80°C vs. a Nafion®112 membrane at 80°C.

The equilibrium uptakes are expressed in terms of average number of water molecules per sulfonic acid group. PCHD membranes absorb considerably more water than Nafion® at each RH at 80°C. The difference is even pronounced at low RH and 80°C which is significant for fuel cell applications. This enhancement is attributed to the influence of PEG in this specific sample and accounts for the higher conductivity although cross-linking is most likely another important factor. It is also interesting to see that the PCHD membrane uptake did not change with increasing temperature from 25 to 80°C.

Thermal Stability. TGA studies were performed on these materials to determine their thermal degradative stability in N₂ atmosphere (no thermo-oxidative effects present). While the temperatures reached in these tests are above fuel cell operating temperature, the degradation temperatures reflect

FIGURE 3. Vapor pressure isotherm at 25 and 80°C for PCHD (copolymer with PEG) based membrane vs. Nafion®112 membrane measured at 80°C.

material cohesion that is related to membrane durability. The information reported here is part of an effort to understand the relationship between conductivity and thermodegradative behavior.

Figure 4 shows mass loss (in N₂ atmosphere) vs. temperature up to 800°C for some representative membranes. Assignment of thermal degradation mass loss events, based on related work reported in the literature [1,2], is as follows: for all samples, except unsulfonated XPCHD_1001, at $\approx 95^\circ\text{C}$, there is mass loss of ~ 5 to 20%. This initial loss is believed to be due to polymer chain depolymerization which proceeds until more thermally stable units on the polymer backbone are reached. The remaining backbone remains thermally stable until 200°C after which more chain depolymerization takes place. Between 200 and 400°C, membrane thermal stability depends on the strength of interactions among SO₃H groups and restrictive crosslinks. Then, the backbone shows more resistance to thermal degradation due to the formation of carbonized compounds, formed from the dehydrogenation of PCHD, which can also be regarded as graphitic compounds formed by the carbonization of phenyl units. This is the reason why most of the samples show a remaining mass of 50 to 60% at the high temperature of 800°C.

Dynamic Mechanical Analysis. Long and short range macromolecular motions in a new membrane batch were identified using DMA and the loss tangent ($\tan \delta$) vs. temperature (T) curves are seen in Figure 5. Many distinct peaks with different degrees of broadening can be observed for both membranes. The breadth of a peak reflects microstructural heterogeneity.

There is a small peak between -120 and -30°C tentatively assigned to local motions of -CH-S-S-CH- crosslinks plus motions of -CH-Cl and -CH-OH side chains because the shortest range motions, which are

FIGURE 4. TGA Thermograms of Some Representative Membranes

FIGURE 5. Tan δ vs. T curves for new membranes compared to an earlier-synthesized membrane.

active at low temperatures, would seem to be possible in these groupings. A very broad peak exists between about -30 and 200°C which is thought to be the glass transition (T_g). This is active at fuel cell operating temperatures but would most likely shift to lower temperature with sorbed water. Based on assignments we reported earlier, crosslinked PCHD films showed $T_g \sim 95^\circ\text{C}$. Finally, there is a small peak above 200°C which is suggested, based on studies of other ionomers, to be due to disruption of $-\text{SO}_3\text{H}$ group aggregates.

The glass transition peak is somewhat broad and there is more than one relaxation active. Perhaps hydrogen bonding interactions among the $-\text{SO}_3\text{H}$ groups which would form physical cross-links might be responsible for broadening the glass transition peak owing to microstructural/chemical heterogeneity. It is not clear, at this point, why the low temperature peak for the XPCHD_1008_SPCHD_101 sample shifts to higher temperature compared to other samples. The glass transition peak for XPCHD_1008_SPCHD_101 is divided into two peaks which is not understood. In comparing samples with (either blending or copolymerization) and without PEG; no change in the three peak positions is noticed although one might expect some plasticization due to the presence of PEG.

The corresponding change in storage modulus (E') with increasing temperature is seen in Figure 6. The initial drop in E' with increasing temperature resembles a glass transition, although it must be said that the drop is less than an order of magnitude. All membranes showed an *increase* in E' beyond around 0°C, which must be explained because this indicates a material stiffening.

This behavior is hypothesized to involve SO_3H group associations which act as physical crosslinks. An increase in thermal mobility of these hydrogen bonding groups above T_g might impart sufficient mobility for

FIGURE 6. Storage modulus (E') vs. temperature for membranes containing PEG vs. an earlier-synthesized membrane without PEG.

them to migrate to form larger energetically-favorable associations which increases E' for the membranes with higher conductivities. The final drop in E' (around 200°C) can be interpreted in terms of the subsequent dissociation of these acid group aggregates as also reflected by the transition peaks in Figure 5. This is of special interest for fuel cell membranes at a temperature around 100°C as mechanical stability is desired in that temperature range.

Conclusions and Future Directions

Work in Year 3 has focused on optimizing the chemistry of membranes based on PCHD homopolymers, polymer blends and block copolymers of PCHD and PEG. A range of membranes with various degrees of crosslinking and sulfonation have been synthesized and characterized for their conductivity, thermal and mechanical stability.

Blending and copolymerization of PEG with PCHD before crosslinking causes a big jump in conductivity most likely through plasticization. This increase was observed at low RH and 120°C in comparison with Nafion® membranes measured at the same conditions. Also, PCHD membranes retain more water than Nafion® at low RH and 80°C. The new batch of membranes have higher proton conductivity than that of Nafion® samples not only at high RH ($\geq 80\%$) but also at low RH (50%). The fact that conductivity obtained for membranes made from a block copolymer of PCHD and PEG was higher than that of Nafion® samples at 50% RH and at 120°C is very encouraging and provides useful information in directing future synthetic efforts.

The Year 2 milestone of demonstrating conductivity of 0.07 S/cm at 80% RH at 30°C has been met. However, further effort is needed to meet the final proton conductivity requirements specified by DOE (conductivity = 0.1 S/cm at 50% RH at 120°C).

We have successfully characterized the thermal stability of these membranes as related to material cohesion that is important for high temperature fuel cell operation. Also, we have determined dynamic mechanical studies of thermal transitions that can be implicated with gas, water and proton transport as well as establish the high temperature stability ceiling of these materials. Proton conductivity tests were performed to rank the feasibility of the various membrane compositions.

Future directions include:

- Further optimize crosslinking and sulfonation conditions for Type 1 membranes to obtain both high proton conductivity and good mechanic strength.
- Change the composition of polymer blends and block copolymers to obtain ideal membrane morphology for higher proton conductivity at lower RH.
- Improve chemical stability by partial aromatization and inorganic sol-gel modification.
- Perform broadband dielectric spectroscopic studies of membranes to probe the nature molecular motions that are active at fuel cell-relevant temperatures and well as the coupling of these motions to water and proton transport.
- Determine the viscoelastic properties of membranes, such as creep, stress relaxation, and cyclic loading with a view toward mechanical durability.
- Once a higher degree of dimensional stability is imparted to these materials, we will render them more hydrophobic to have higher temperature water retention by growing, in situ, by sol-gel processes, inorganic oxide nanostructures. This will additionally improve the mechanical durability.
- Prepare MEAs and test their performance as well as exposing them to OCV test to check their durability and life time. Chemical degradation of type 1 membranes via Fenton's reagent. And then, characterization of degraded samples via both chemical and OCV procedures using broadband dielectric spectroscopy.

Special Recognitions & Awards/Patents Issued

1. "Copolymers of Fluorinated Polydienes and Sulfonated Polystyrene", CIP of USP 11/906,118 (patent pending).
2. We were recently awarded \$75,000 by the Tennessee Technology Development Corporation to continue development and commercialization of these membranes for a variety of applications.

FY 2009 Publications/Presentations

1. "Novel Ion-Containing Polymers Via Post-Polymerization Chemistry: Synthesis, Morphology, and Mineralization Studies", J.W. Mays, invited lecture at the 7th Hellenic Polymer Conference, September 28 – October 1, 2008, Ioannina, Greece.
2. "Sulfonated Fuel Cell Membrane", J. Mays, S. Deng, K. Mauritz, M. Hassan, presented at the Tennessee Innovation Conference, Nashville, TN, November 20–21, 2008.
3. "Novel Charged Polymers: From Biomineralization to Fuel Cell Membranes", J.W. Mays, invited lecture at the University of Minnesota, Department of Chemical Engineering and Materials Science, December 2, 2008.
4. "Poly(cyclohexadiene)-Based Polymer Electrolyte Membranes for Fuel Cell Applications", J. Mays, S. Deng, M. Hassan, and K. Mauritz, presented at US Car, Detroit, MI, February 11, 2009.
5. "Poly(cyclohexadiene)-Based Polymer Electrolyte Membranes for Fuel Cell Applications", J. Mays, S. Deng, M. Hassan, and K. Mauritz, presented to Department of Energy, Washington, D.C., February 26, 2009.
6. "Novel Charged Polymers: From Biomineralization to Fuel Cell Membranes", J.W. Mays, invited Bayer Lectures on Polymers, Cornell University, Ithaca, New York, April 8, 2009.
7. "Poly(cyclohexadiene)-Based Polymer Electrolyte Membranes for Fuel Cell Applications", J. Mays, S. Deng, M. Hassan, and K. Mauritz, presented at the DOE Annual Hydrogen Review, Arlington, VA, May 18–21, 2009.

V.D.5 High Temperature, Low Relative Humidity, Polymer-type Membranes Based on Disulfonated Poly(arylene ether) Block and Random Copolymers Optionally Incorporating Protonic Conducting Layered Water Insoluble Zirconium Fillers

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Project State Date: May 1, 2006
End Date: September 30, 2009

- Determine the hydrophilic-hydrophobic block length effect on the formation of nanophase separated morphologies.
- Provide a clearer understanding about the structure/property relationship of the hydrocarbon-based PEMs.
- Establish the effects of solution-casting conditions (solvent type, film drying temperature, and solvent removal rate) on the final morphology and properties of block polysulfone ether polymers-bi phenyl sulfone (BPSH-BPS) multiblock copolymer PEMs for the optimization of the casting process.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) Durability
- (B) Cost
- (C) Performance

Technical Targets

- Area specific resistance of 0.02 ohm-cm² at 120°C and P_{H₂O} of 40-80 kPa, corresponds to a conductivity of 0.1 S/cm for a 20 micron thick membrane.

Accomplishments

- Novel methodologies for the synthesis of hydrophilic-hydrophobic block copolymers without sequence randomization were developed by utilizing highly reactive perfluorinated small molecules as linkage units.
- Reactive hydrophilic oligomers were successfully coupled with reactive hydrophobic oligomers to make tough film forming compositions with good mechanical strength and conductivities either in liquid water or as a function of RH which are as good as or better than the Nafion[®] benchmark controls.
- Fundamental membrane properties including ion exchange capacity (IEC), water uptake, and hydration number (λ) were characterized with the hydrophilic-hydrophobic multiblock copolymers.

Objectives

Develop a superior material for polymer electrolyte membranes (PEMs), which will meet performance requirements associated with higher temperatures and lower relative humidities (RHs) by the year 2010.

- The new materials will outperform the present standard material, Nafion[®].
- The work builds upon earlier results from VT wherein thermally, oxidatively, hydrolytically stable tough high T_g ion-containing copolymers based on polyarylene ethers were successfully used as PEM systems under relatively high humidity conditions.
- Current objectives are to synthesize and characterize hydrophilic-hydrophobic sequenced block copolymers based upon high performance polymer materials as an approach to develop performance criteria at high temperatures and low RH.

- Morphologies of the hydrophilic-hydrophobic multiblock copolymers were investigated and well-defined nanophase separated morphology was obtained with longer block lengths copolymers.
- Through chemical structure and processing methodology reached the DOE goal of 70 mS/cm at 80% RH and 30°C.

Introduction

The goal of this research is to develop a material suitable for use as a PEM which by the year 2010 will meet all the performance requirements associated with fuel cell operation at high temperatures and low RH, and will out-perform the present standard Nafion®. In particular, it is our objective to extend our previous research based on the use of thermally, oxidatively, and hydrolytically, ductile, high Tg ion containing polymers based on poly(arylene ethers) to the production of polymer electrolyte membranes which will meet all the performance requirements in addition to having an areal resistance of <0.02 ohm-cm² at a temperature of up to 120°C, RH of 25 to 50%, and up to 2.5 atm total pressure. In many instances, our materials already out perform Nafion®, and it is expected that with some modification by either combining with conductive inorganic fillers and/or synthesizing as a block copolymer it will meet the performance criteria at high temperatures and low RH. A key component in improving the performance of the membranes (and in particular proton conductivity) and meeting the cost requirements of \$40/m² is our development of a film casting process, which shows promise for generation of void free thin films of uniform thickness with controlled polymer alignment and configuration.

Results

Hydrophilic and hydrophobic telechelic oligomers with controlled molecular weight were synthesized via step-growth polymerization. The hydrophilic oligomers were fully disulfonated poly(arylene ether sulfone)s (BPS100) and the hydrophobic oligomers were partially fluorinated poly(arylene ether ketone)s (6FK). The fluorination of the hydrophobic segment is expected to promote nanophase separation with the hydrophilic segment, resulting in improved proton transport properties. The phenoxide terminated 6FK hydrophobic oligomers were then end-capped with hexafluorobenzene (HFB) to facilitate a coupling reaction with the phenoxide terminated BPS100 hydrophilic blocks. Multiblock copolymers with various block lengths were synthesized by coupling the phenoxide terminated BPS100 and the HFB end-capped

6FK oligomers (Figure1). The coupling reaction was conducted at 105°C, which was low enough to prevent possible trans-etherification.

Four BPSH-6FK multiblock copolymers with different block lengths were systematically synthesized and their fundamental membrane properties were evaluated, which are summarized in Table 1, along with values for the control PEM materials, Nafion® 112 and biphenyl based disulfonated polysulfone (35% saturation; BPSH35). The intrinsic viscosity of the copolymers ranged from 0.62 to 0.88 dL/g, which was sufficiently high to obtain tough ductile membranes. As expected, the water uptake results for the multiblock copolymers were shown to be strongly dependent on their IEC values, which is associated with increased ionic moieties in the system. In addition to the impact of IEC, the water uptake behavior of the multiblock copolymers was also strongly influenced by hydrophilic and hydrophobic block lengths. Specifically, the water uptake values for the multiblock copolymers with similar IECs increased with increasing block length. For example, the BPSH3-6FK3, BPSH5-6FK5, and BPSH10-6FK10 copolymers displayed very similar IEC values of around 1.5 meq/g. If water uptake is exclusively dependent on IEC, then the water uptake values for these copolymers should have been very similar. However, our results showed that water uptake was strongly influenced by the hydrophilic and hydrophobic block lengths, which increased from 31% for the BPSH3- 6FK3, to 81% for the BPSH10- 6FK10. It should be noted that while the BPSH15- 6FK15 displayed somewhat lower IEC (1.34 meq/g) than other equal length block copolymers, its water uptake was even higher than that of the BPSH10-6FK10.

FIGURE 1. Synthesis of Segmented Sulfonated Multiblock Copolymers (BPSH-6FK) with HFB Linkage Group

TABLE 1. Fundamental Membrane Properties

Copolymers	Experimental IEC (meq g ⁻¹) ^a	Intrinsic Viscosity (dL g ⁻¹) ^b	Water Uptake (%)	Conductivity (S cm ⁻¹) ^c	Hydration Number (λ)
Nafion [®] 112	0.90	-	25	0.090	15.0
BPSH 35	1.50	0.70	36	0.070	13.3
BPSH 3 – 6FK 3	1.51	0.78	31	0.08	12
BPSH 5 – 6FK 5	1.53	0.62	69	0.10	25
BPSH 10 – 6FK 10	1.48	0.88	81	0.11	30
BPSH 15 – 6FK 15	1.34	0.70	100	0.12	41

^a Determined by titration with NaOH.^b In N-methylpyrrolidone with 0.05 M LiBr at 25°C.^c Measured in deionized water at 30°C.

Figure 2 shows the relationship between temperature and the proton conductivity of the fully hydrated multiblock copolymers. As clearly demonstrated, proton conductivity increased with increasing temperature, reaching 185 mS/Cm at 80°C for the BPSH10-6FK10. Moreover, the conductivity-temperature slope for each of the copolymers is similar, implying that the copolymers have a similar conduction mechanism. Compared with Nafion[®] 112, the multiblock copolymers displayed a slightly lower temperature dependence on proton conductivity.

Proton conductivity as a function of RH at 80°C was also studied. As shown in Figure 3, the proton conductivity of the BPSH35 random copolymer dropped rapidly at lower RH values. Although BPSH35 demonstrated acceptable proton conductivity under fully hydrated conditions on account of sufficient water content, its proton conductivity under partially hydrated conditions decreased significantly due to the scattered

hydrophilic domains in the random copolymer. In short, the absence of the hydrophilic domain connectivity and insufficient water content in the membrane was unable to maintain high proton conduction under partially hydrated conditions. Conversely, the performance of the multiblock copolymers under partially hydrated conditions was shown to be superior to the random copolymer, and also improved with increasing block lengths. For example, the conductivity of the BPSH15-6FK15 under partially hydrated conditions was comparable to that of Nafion[®] 112.

Figure 4 shows transmission electron microscopy (TEM) images of the BPSH-6FK multiblock copolymers with different block lengths. The bright and dark regions in the images correspond to the hydrophobic and hydrophilic segments, respectively. Although no distinct phase-separation was observed for the BPSH5-6FK5 system (Figure 4 (a)), enhancements in connectivity of hydrophilic domain were found in longer block lengths multiblock systems (Figure 4 (b)). Further increase in the block length resulted in higher degree of phase separation showing a clear lamellar morphology (Figure 4 (c)). Thus, by utilizing the well-connected hydrophilic regime for proton conduction, improved

FIGURE 2. Proton Conductivities of BPSH-6FK and Nafion[®] 112 in terms of Temperature **FIGURE 3.** Proton Conductivities of BPSH-6FK and Nafion[®] 112 under Partially Hydrated Conditions at 80°C

FIGURE 4. TEM Phase Images of BPSH-6FK Multiblock Copolymers (a) BPSH5-6FK5, (b) BPSH10-6FK10, and (c) BPSH15-6FK15

proton conductivity under partially hydrated conditions was achieved.

Conclusions

- Novel multiblock copolymers were synthesized by coupling fully disulfonated poly(arylene ether sulfone) and partially fluorinated poly(arylene ether ketone) as hydrophilic and hydrophobic oligomers, respectively.
- To minimize a possible sequence randomization during the coupling reaction, the highly reactive perfluorinated small molecule, HFB, was utilized as a linkage group.
- The copolymers produced tough ductile membranes via dimethylacetamide solution casting. Resulting proton conductivity and water uptake measurements revealed that changes in hydrophilic and hydrophobic block length influenced membrane properties at similar IEC values by forming nanophase separated morphologies.
- The multiblock copolymer membranes showed highly anisotropic swelling behaviors in comparison to the random copolymers, which were isotropic.
- Utilization of a selective solvent, dimethyl acetamide, yielded the microstructures with more ordered and longer-range lamellar ionic domains, resulting in considerable increase in both water uptake and proton conductivity of the BPSH-BPS multiblock copolymer PEM.
- Drying temperature and/or solvent removal rate also turned out to be a critical factor for the performance of a PEM.

Future Directions

- Synthesis of multiblock copolymers with enhanced hydrophilic-hydrophobic contrast by utilizing more hydrophilic oligomers for sharper phase separations.
- Development of crosslinked PEM system with higher IEC to manage swelling and water uptake behavior.
- Further investigation on the effects of solution-casting conditions using dimethylformamide and dimethylsulfoxide, which show different degrees of

selectivity, and multiblock copolymers consisting of different block lengths, e.g., BPSH-BPS (10k-5k, 15k-10k, 5k-10k, and 10k-15k).

FY 2009 Publications/Presentations

1. Hae-Seung Lee, Abhishek Roy, Ozma Lane, Stuart Dunn, and James E. McGrath, "Hydrophilic-hydrophobic multiblock copolymers based on poly(arylene ether sulfone) via low temperature coupling reactions for proton exchange membrane fuel cells", *Polymer*, 49 (2008), 715-723.
2. Hae-Seung Lee, Abhishek Roy, Ozma Lane, and James E. McGrath, "Sulfonated Fluorinated Multiblock Copolymers with Hydrophilic-Hydrophobic Sequences for Proton Exchange Membranes", 213th ECS Meeting, May 18-22, 2008, Phoenix, Arizona.
3. Hae-Seung Lee, Ozma Lane, and James E. McGrath, "Synthesis and characterization of multiblock copolymers with hydrophilic-hydrophobic sequences for proton exchange membranes. 236th ACS National Meeting, Philadelphia, PA, August 17-21, 2008 (2008).
4. Lee M, Park J, Lee H-S, Lane O, Moore RB, McGrath JE, Baird DG, Effects of solution-casting conditions on the final morphology and properties of disulfonated poly(arylene ether sulfone) multiblock copolymer films for proton exchange membranes, *Polymer*, submitted.
5. Lee M, Lane O, Lee H-S, McGrath JE, Baird DG, Effects of molecular structure and solution-casting conditions on the final morphology and properties of disulfonated poly(arylene ether sulfone) copolymer films for proton exchange membranes, 2008 American Institute of Chemical Engineers Annual Meeting, November 16-21, Philadelphia, Pennsylvania.

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1. Anand Badami, Ozma Lane, Hae-Seung Lee, Abhishek Roy, and James E. McGrath, "Fundamental investigations of the effect of the linkage group on the behavior of hydrophilic-hydrophobic poly(arylene ether sulfone) multiblock copolymers for proton exchange membrane fuel cells" *Journal of Membrane Science* (2009).
2. Abhishek Roy, Xiang Yu, Stuart Dunn, and James E. McGrath, "Influence of microstructure and chemical composition on proton exchange membrane properties of sulfonated-fluorinated, hydrophilic-hydrophobic multiblock copolymers" *Journal of Membrane Science* (2009), 327(1+2), 118-124.
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V.D.6 Protic Salt Polymer Membranes: High-Temperature Water-Free Proton-Conducting Membranes

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Contract Number: DE-FG36-06G016029

Subcontractor:
Wiley Young, University of Akron, Akron, OH

Project Start Date: January 15, 2006
Project End Date: January 14, 2011

Objectives

The project objective is to make new proton-conducting solid polymer electrolyte membrane (PEM) materials with the following properties:

- High proton conductance at high temperature (-40 to up to 120°C).
- Effectively no co-transport of molecular species with proton.
- Reduction of fuel cell overvoltage.
- Durable, good mechanical strength and chemical stability.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Program Plan:

- (A) Durability
- (C) Electrode Performance.

Technical Targets

The DOE goal is to make a stable electrolyte membrane that has a proton conductivity greater than 0.1 S/cm at 120°C when supplied gases with low 25 to 50% relative humidity (RH) and greater than 0.0005 S/cm at -40°C.

Accomplishments

The DOE targets and summary of the major works and accomplishments in 2009 for achieving the DOE technical targets are summarized in Table 1.

TABLE 1. Progress towards meeting technical targets for making a proton-conducting high-temperature polymer electrolyte membrane (HT PEM).

Item	Description
DOE targets	Make a membrane with conductivity of 0.1 S/cm at 0 to 50% RH at 120°C. Determine and report best membrane conductivity by February 2009
Summary of ASU work	Liquid and polymeric high-temperature proton-conducting protic salt membranes were made and tested for conductivity and stability in fuel cell conditions, namely: (i) pILs protic ionic liquids, and (ii) pIMs protic ionic membranes with non-leachable salt moieties. Selected new membranes were sent to Beektech for external validation of conductivity at various temperatures and RH conditions.
Accomplishments Feb-09	A neat indium tin phosphate (ITP) membrane was made that has conductivity 0.16 S/cm from 25°C to greater than 120°C and 0% RH. Crossover in pure ITP membrane eliminated by blending 70 wt% ITP with 30 wt% of a proton conducting organic polymer (polyvinyl pyridinium phosphate, PVPP) but at a cost of reduced conductivity.

Introduction

A membrane that conducts protons up to 120°C without the need for water would allow for a more efficient, compact and lighter weight PEM fuel cell. Presently PEM fuel cell electrolyte membranes need water as an ionizing solvent. Consequently, this requires operation below 80°C, complex humidifiers to retain solvent water, large radiators to reject waste

heat and lowers the performance of platinum catalysts because, at high potentials in the presence of solvent water, platinum oxides form that inhibit air cathode activity, so that fuel cell efficiency drops from the theoretical 95% to no higher than ~65%. These deficiencies present formidable barriers to the use of fuel cells as power sources. The project aims to make a membrane with anhydrous proton-containing salts to conduct protons from -40 to 120°C and to study the fundamental mechanism of proton conduction in these salt membranes. At ASU it was discovered that neat protic ionic liquid (pIL) electrolytes and crystalline solid versions have high proton conductivities from ambient temperatures to over 200°C. A salt electrolyte forms when a proton is transferred from a Brönsted acid to a Brönsted base. The high proton conductivity of a protic salt evidently results from the rotational freedom of the nearly symmetrical constituent ions and from having an optimal difference in pKa of the acid and base.

Approach

The approach has two parts: synthesis of membranes and characterization of the membranes for conductivity, stability and mechanism of proton conduction.

Proton-conducting PEMs are being made based on concepts developed with pILs. The pILs are used to model membranes to help select acid and base moieties. Polymers, acids and bases have been varied to optimize proton conduction, stability and other PEM properties. The liquid and solid membrane salt-electrolytes are characterized for proton conductivity by electrochemical impedance spectroscopy (EIS) in thermostatted cells and for stability by thermal gravimetric analysis and by monitoring fuel cell performance in time. The mechanism of the transport of protons, anions, and molecules is being investigated by three nuclear magnetic resonance (NMR) methods: 1) pulse field gradient NMR to measure the diffusivity of ions in liquid and solid states, 2) multipulse solid-state NMR to measure the molecular motion and interactions of species in solid membranes, and 3) electrochemical NMR to measure distribution of species during proton conduction in solid membranes.

Results

The team has been developing new water-free proton-conducting salt membranes. Electrolytes made to date include: the liquid salts, called pILs, polymeric salt membranes with (leachable) and without (non-leachable) pILs added, and solid ceramic membranes of non-stoichiometric ITP ($\text{In}_{0.1}\text{Sn}_{0.9}\text{P}_2\text{O}_7$) alone as well as ceramic blended with a non-leachable organic salt PVPP.

Types of salt electrolytes made to date:

1. Protic ionic liquids (pILs).
2. Polysiloxane (PS) solid PEMs.
3. PS PEMs filled with pILs.
4. Cellulose PEMs filled with pILs.
5. PVPP PEMs.
6. ITP ceramic PEMs.
7. PVPP and ITP blended PEM.
8. Phosphazene trimer (PT) – polyimide (PI) blended PEMs.
9. Polyphosphazene (PP) – PI-blended PEMs.

The best membranes from the standpoint of conductivity were polymers filled with pILs and ceramic ITP membranes [2]. Polymer membranes filled with pILs have conductivity approaching the DOE Go/No-Go targets. Insoluble ceramic membranes made from ITP have proton conductivity over a broad temperature range that apparently exceeded the DOE Go/No-Go targets (Figure 1).

Studies of pILs have helped understand and develop solid proton-conducting ionic membrane electrolytes (pIMs). As seen in Figure 2, the conductivity for the solid poly vinyl pyridinium phosphate ($\text{PVP-H}_3\text{PO}_4$) membrane is high even in the absence of water at high temperatures. This high conductivity (measured by EIS) is attributed to close proximity of one pendant salt group to another, so that protons can be passed by direct contact of these salt groups. Precisely how protons are passed is the subject of ongoing NMR studies. Although the PVPP has high proton conductivity, Figure 2 shows that it is not quite as high as for the analogous liquid vinyl pyridinium phosphate pIL ($\text{Py-H}_3\text{PO}_4$) or 2-fluoro pyridinium triflate (2-FPyTf) as a function of

FIGURE 1. Conductivity determined by impedance spectroscopy for three electrolyte samples as a function of temperature. Electrodes E-Tek Pt/C (0.5mg/cm²) fed dry: H₂ gas, T=25 to 275°C. Solid triangle: Solid membrane of poly vinyl pyridinium phosphate (PVP-H₃PO₄), Solid diamond: solid ceramic membrane of pure 10%indium 90%ITP. Solid square: a solid membrane of 70% ITP blended with 30 wt% PVP- H₃PO₄.

FIGURE 2. Conductivity determined by impedance spectroscopy for three electrolyte samples as a function of temperature. Electrodes E-Tek Pt/C (0.5mg/cm²) fed dry: H₂ gas, T= 25 to 150°C. Solid triangle: Solid poly vinyl pyridinium phosphate (PVP- H₃PO₄) membrane, Open diamond: Liquid vinyl pyridinium phosphate pIL (P- H₃PO₄), Open square: Liquid 2-fluoro pyridinium triflate (2-FPyTf).

temperature. This is expected, as the polymer forbids proton conduction by salt translation and restricts conduction to “hopping” only. Fuel cell, hydrogen pumping and water electrolysis were done in cells using PVPP as the cell membrane, and these experiments were steady in time (for as long as days) which is only possible if proton is hopping in PVPP.

The best membranes from the standpoint of conductivity were made from pure and blended ITP and have conductivity apparently exceeding the DOE Go/No-Go targets (Figure 1). Figure 3 shows preliminary fuel cell performance for these two membranes. The highest power is with the pure ITP but the highest open circuit voltage is with the ITP blended with PVPP polymer. This later improvement is most likely due to decreasing of gas crossover when the pores of the porous ITP membrane are filled by PVPP polymer.

Conclusions and Future Directions

- Protic salt electrolytes do not require water to conduct protons and behave like non-aqueous electrolytes even with 20% water, because water is dispersed in the pIL and its reactivity is not like “bulk” water
- The absence of bulk water reduces formation of Pt-OH on the Pt surface, accounting for the observed lower overpotential for oxygen reduction, higher cell efficiency, and possibly lower corrosion and Pt particle growth.
- Status of pILs
 - Fluorinated 2-fluoropyridinium triflate (2-FPTf) and non-fluorinated pyridinium phosphate are two new non-aqueous pIL electrolytes that gave high proton conductivity and good stability.

FIGURE 3. Fuel cells made with a pure ITP membrane (top) and a membrane with an ITP/PVPP blend (bottom).

- 2-FPTf is a non-aqueous proton-conducting pIL with higher hydrogen/oxygen fuel cell performance than aqueous 85% phosphoric acid as electrolyte.
- Status of pIMs
 - PVPP gives a non-aqueous membrane electrolyte that has temporally stable and high proton conductivity, but not as high as liquid PP.
 - Syntheses of similar water insoluble poly phosphazene membranes are in progress.
 - ITP has higher proton conductivity than the DOE target, and when blended with polymeric PVPP, gives no H₂/O₂ crossover but at the expense of conductivity.

The planned work for next year and anticipated accomplishments are to:

- Make PEMs based on:
 - ITP with different ratios of non polar (VITON) and ionic (PVPP) polymer binders and test for proton conductivity and fuel cell performance.
 - PPs with pendant azoles and reacted with fluorinated acid to give tough flexible non-leachable PEMs with all acid and base moieties

- to be immobilized by covalent and electrostatic binding.
- Screen activity of non-platinum catalysts for promoting oxygen electroreduction in new fluorinated PILs.
- Use electrochemical NMR (eNMR) to characterize proton conductivity in membranes. NMR will be used to study solid membranes:
 - to investigate motions during proton conduction by 2-dimensional NMR.
 - to investigate distribution of species during different levels (currents) of proton conduction by eNMR Hittorf method.
- Use electrochemical Fourier transform infrared spectroscopy and possible X-ray of the Pt surface in PIL electrolytes to investigate:
 - Pt oxide formation as a function of potential and electrolyte composition.
 - adsorption of electrolyte on Pt as a function of electrode potential.

4. “Characterization of Poly(dichlorophosphazene)s and their reactions to Poly(organophosphazene)s”, Alyson Leigh; Sujeewani Ekanayake; Supat Moolsin; Matthew Panzer; Wiley Youngs; Claire Tessier; Chrys Wesdemiotis, The University of Akron, Akron, OH, Mass Spectroscopy Society Meeting, Session: Materials and Polymers - Poster Hall Code: WPJ Time Slot/Poster Number: 217 June 2008.

5. “Study of Transport Properties of Trifluoromethanesulfonic acid monohydrate: Diffusivity, Conductivity and Viscosity, Mohammed Abdullah”, M.S. Thesis, Physics Department, Arizona State University, April, 2008.

6. “Characterization of protic ionic liquids: NH chemical shift”, J.-P. Belieres in the I&EC division, Paper no. 82, Am. Chem. Soc., Philadelphia, PA (2008). “Efficient Water Electrolysis in Protic Ionic Liquids”, Jeffery Thomson, Jean-Philippe Belières, C. Austen Angell and Don Gervasio, 214th Meeting of the Electrochemical Society, Honolulu, Hawaii, October 12–17 (2008).

7. “Protic ionic liquids as probes for acidity of superacids”, in preparation.

Special Recognitions & Awards/Patents Issued

1. “Stable Protic Ionic Liquid (pIL) Fuel Cell Electrolytes”, Gordon Research Conference, Bryant College, Rhode Island, July 20, 2008. Accompanying poster presentation on July 23, 2008 was awarded one of 3 “Best GR Conference Posters”.
2. “Electrochemistry in Ionic Liquid Electrolytes”, Invited talk to the Chemical and Biochemical Engineering Department, Graduate Seminar Series, North Carolina State University, August 25, 2008.
3. “Electrochemistry in Ionic Liquid Electrolytes”, Invited talk to University of Warsaw, March 27, 2009, Warsaw, Poland.
4. “Electrochemistry in Ionic Liquid Electrolytes”, Invited talk to the 7th Spring Meeting of the ISE, Szczyrk, Poland March 23, 2009.

References

1. “Anhydrous Proton-Conducting Polymeric Electrolytes for Fuel Cells”, S.R. Narayanan, Shiao-Pin Yen, L. Liu, and S.G. Greenbaum, J. Phys. Chem. B 2006, 110, 3942-3948.
2. “Intermediate-Temperature Proton Conduction in Al³⁺-Doped SnP₂O₇”, A. Tomita, N. Kajiya, T. Kamiyama, Masahiro Nagao, and Takashi Hibino, Journal of The Electrochemical Society, 154, B1265-B1269 (2007).

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1. “High Temperature Fuel Cells using Ionic Polysiloxane Membranes”, With and Without Ionic Plasticizers, X. Sun, D. Gervasio and C. Angell (Arizona State University) Paper Number 442, 213rd Meeting of the ECS, May 18–22, 2008 Phoenix, AZ.
2. “On the State of the Proton in Protic Ionic Liquids”, J. Belieres, N. Byrne, D. Gervasio and C. Angell (Arizona State University) Paper Number 464, 213rd Meeting of the ECS, May 18–22, 2008 Phoenix, AZ.
3. “Stable Protic Ionic Liquid (PIL) Fuel Cell Electrolytes”, J. Thomson, R. Marzke and D. Gervasio (Arizona State University) Paper Number 466, 213rd Meeting of the ECS, May 18–22, 2008 Phoenix, AZ.

V.D.7 Fluoroalkylphosphonic-Acid-Based Proton Conductors

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Contract Number: DE-FG36-06GO16031

Subcontractor:
University of Utah, Salt Lake City, UT

Project Start Date: April 2006
Project End Date: March 2011

Objectives

- Synthesize and characterize new proton-conducting electrolytes based on the fluoroalkylphosphonic acid functional group; and
- Perform quantum chemistry and molecular dynamics simulation studies of fluoroalkylphosphonic acid-based electrolytes.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section (3.4.4) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) Durability
- (C) Performance
- (E) System Thermal and Water Management

Technical Targets

The following technical targets from Table 3.4.11, Membranes for Transportation Applications, from the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan, as revised April 27, 2007, are relevant to this project:

- Membrane ionic conductivity >0.10 S/cm at $<120^{\circ}\text{C}$ and water partial pressure of 1.5 kPa for transportation applications (2010 target).
- Area specific resistance <0.02 ohm cm^2 under similar conditions.

Accomplishments

- Completed synthesis and characterization of fluoroalkyl phosphonic and difluoroalkyl phosphinic acid (FPA) model compounds.
- Measured proton conductivity of FPA and other (fluoroalkyl-sulfonic and -carboxylic) acid model compounds under dry (anhydrous) and wet (variable number of waters per acid) conditions. FPAs show highest anhydrous conductivity of all model acids tested.
- Measured $^1\text{H}^+$ and ^{19}F self-diffusion coefficients for neat acids by pulsed-field gradient-nuclear magnetic resonance (PFG-NMR). Higher diffusivity for $^1\text{H}^+$ indicates that proton hopping occurs in FPAs but not for other acids.
- Correlations of conductivity and diffusivity with viscosity support this conclusion.
- ^{31}P NMR spectra reveal absence of pyrophosphates in neat FPA samples, suggesting that FPA dehydration does not occur to any appreciable extent.
- Born-Oppenheimer Molecular Dynamics (BOMD) and Q-HOP MD (a molecular dynamics simulation that includes quantum chemistry calculations) simulations support the conclusion that proton hopping occurs in neat FPA samples but not in other model acids.
- Simulations also show domain/proton transport network formation in some FPA samples but not others. Domains are small and incomplete in samples with a low mass fraction of acid and a high mass fraction of fluoroalkyl groups.
- Continued synthesis of FPA ionomers having a range of structures including some with protecting groups to enable processing as membranes prior to deprotection to make acids.

- Imaged ionomer domain structure by transmission electron microscopy (TEM) with Pb^{2+} staining; difluoroalkyl phosphonic acid ionomers shown to have smaller protonic domains than fluoroalkyl phosphonic acid ionomers.
- Conductivity values for FPA membranes were measured and are below milestones but are steadily improving.

Introduction

This research is focused on synthesis, characterization, and computer simulation and quantum chemistry studies of proton conduction in a family of fluoroalkylphosphonic-acid-based comb-branch ionomers and related small molecules which comprise liquid-phase electrolytes. The target materials are excellent candidates for use in high-temperature (120°C) low-humidity (25-50% relative humidity) polymer electrolyte fuel cell (PEFC) power sources for transportation applications. The target ionomers will contain no water-soluble components; therefore, they will be able to withstand repeated contact with liquid water, as is inevitable in a transportation PEFC that will experience frequent start-up and shut-down cycling.

Approach

We are following a dual approach involving synthesis and characterization of FPA electrolytes focusing on ion conduction under a wide range of conditions of temperature and water content (humidity), coupled with computer modeling work that will help explain whether and how proton transport can be facilitated by a Grotthuss-like hopping mechanism, and how the membrane morphology/cluster structure is important in proton transport. The synthesis part focuses on small-molecule FPAs, trifluorovinyl ether (TFVE) FPA monomers, and FPA ionomer membranes prepared by co-polymerization of TFVE monomer with tetrafluoroethylene. Characterization focuses on molecular structure and ionic conductivity at variable temperature and water content.

The modeling portion of the project is expected to provide insight into material structure and proton transport and ultimately guide synthesis of novel FPA-based ionomers. Quantum chemistry calculations of FPA/water clusters will provide water structure, the number of waters needed to deprotonate FPA acid and binding energies. Density functional theory-based BOMD simulations focus on proton transport occurring in small simulated systems (tens of small FPA oligomers) during ~ 10 ps simulations. Classical molecular dynamics simulations without explicit proton hopping provide transport properties and structural information

such as hydrogen bonding networks occurring in larger simulation cells and routinely access tens of nanosecond simulation times. Molecular dynamics (MD) simulations utilizing explicit proton hopping (MS-EVB and Q-HOP) will focus on FPA conductivity and proton transport.

Results

Figure 1 presents anhydrous conductivity data for FPA and other fluoroalkyl model acid compounds over a range of temperatures from 50 to 120°C . Conductivities are high for all acids except the carboxylic acid, however they are highest for the two FPA compounds. Viscosity measurements on the model compounds (data not shown) reveal that the FPA compounds have the highest viscosity, but also the highest conductivity. This is a counterintuitive result which strongly suggest a role for structure diffusion (i.e. proton hopping) in the FPA model compounds, but not in any of the other model compounds. Measurements were also acquired on samples having various amounts of water intentionally added (data not shown). In general, and as expected from prior work, adding water to acid samples always increased conductivity, by a combination of promotion of proton dissociation, proton hopping in the water phase, and lowering of viscosity.

Structure diffusion/proton hopping in neat acids can be quantified by independently measuring the self-diffusion coefficients for the acidic proton and the conjugate base. Such a measurement can be made by PFG-NMR spectroscopy of $^1\text{H}^+$ and ^{19}F self-diffusion coefficients for fluoroalkyl-substituted model acid compounds. Table 1 presents data acquired in this manner for all the model compounds studies in this work. The highlighted areas show the ratio of proton to fluorine self-diffusion coefficients; a ratio above 1

FIGURE 1. Anhydrous conductivity data for FPA and other fluoroalkyl model acid compounds over a range of temperatures from 50 to 120°C .

TABLE 1. Proton and fluorine self-diffusion coefficients for neat samples of fluoroalkyl-substituted acid model compounds obtained from PFG- NMR experiments (left portion of table) and from Q-HOP computer simulations (right portion of table).

Compound	Experiments; at 85°C			Simulation; 85°C	
	$10^{10}D(\text{H}_{\text{OH}})$	$10^{10}D(\text{F}_{\text{Rf}})$	$D(\text{H}_{\text{OH}})/D(\text{F}_{\text{Rf}})$	$10^{10}D(\text{H}_{\text{CF}_3})$	$D(\text{H}_{\text{OH}})/D(\text{F}_{\text{Rf}})$
$\text{CF}_3\text{PO}(\text{OH})_2$	1.12	0.50	2.25	0.98	2.1
$(\text{CF}_3)_2\text{POOH}$	9.47	5.99	1.58	--	--
$\text{CF}_3\text{SO}_3\text{H}$	10.8	10.7	1.00	--	--
CF_3COOH	33.0	33.0	1.00	--	--
$\text{C}_4\text{F}_9\text{PO}(\text{OH})_2$	0.26	0.14	1.94	--	--
$\text{C}_4\text{F}_9\text{SO}_3\text{H}$	4.87	4.87	1.00	--	--
$(\text{C}_4\text{F}_9)_2\text{PO}(\text{OH})$	0.14	0.12	1.17	--	--

indicates a contribution from proton hopping/structure diffusion to proton transport. Ratios above 1 were obtained only for the FPA acids; fluoroalkyl-sulfonic and -carboxylic acids showed no evidence of proton hopping. These results suggest that ionomers containing high concentrations of FPA groups could have high conductivity under conditions of low water availability.

Table 1 also includes a column showing a calculated ratio of proton to fluorine self-diffusion coefficient for one model acid, $\text{CF}_3\text{P}(\text{O})(\text{OH})_2$. The magnitude of the fluorine self-diffusion coefficient from the Q-HOP simulation agrees with experiment to within a factor of

two, and the ratio of proton to fluorine self-diffusion coefficient is in excellent agreement with experiment. This finding validates the model and suggests that it could be used with other structures to predict proton hopping rates for new structures not yet synthesized.

Figure 2 presents structures for several FPA-containing ionomers that were synthesized and studied in the reporting period. The compounds in red squares were studied in particular depth, including measurements of conductivity for membrane samples at variable temperatures and relative humidities. Of particular note are compounds P-26, P-27 and P-29, which have a hydrolyzable protecting group on one of the FPA acid groups. Ionomers with this protecting group in place are processible into membranes which is an advance over FPA ionomers without protection which up to now have been difficult to process.

Conductivity data have been acquired for samples of nearly all the compounds shown in Figure 2. A full discussion of these data is beyond the scope of this report; however, the data can be summarized by noting that samples have not yet been prepared which show conductivities that meet or exceed the technical targets for this project. The reasons for this finding are still not fully clear, given the promising results from the model compounds. Possible contributing factors could include the following: low acid content in ionomers (lower than in the model compounds); poor water uptake in ionomers; and too much/too little crosslinking ionomers which could inhibit formation of domains suitable for

FIGURE 2. Structures of FPA-containing ionomer materials prepared in the reporting period.

FIGURE 3. TEM images of two FPA ionomers and a Nafion® (1,100 equivalent weight) sample. Ionomers were stained by substituting protons for lead ions prior to imaging to provide better TEM image contrast.

rapid proton conduction. Another consideration is the polymer structure itself, particularly the molecular weight and the variation in equivalent weight with reaction progress during the course of ionomer synthesis. It seems likely that, were the project to continue, consistent improvements would be made in the synthesis methods used to make ionomers, which would produce materials having higher molecular weight, improved homogeneity in molecular weight and equivalent weight, and reduced “blockiness” in copolymers resulting in less brittle and more processible materials that would produce membranes having more well-formed ionic domains, and therefore higher conductivity.

Figure 3 shows TEM results which illustrate the domain structures which form for two of the ionomers from Figure 2. A sample of 1,100 equivalent weight Nafion® is also shown for comparison. The images reveal that the fluoroalkylphosphonic acid ionomer (P-27) has a domain structure similar to that of Nafion®, whereas the fluoroalkylphosphonic acid ionomer (P-18) has much smaller and less well formed domains. This is a curious finding since the larger domains should correlate with higher protonic conductivity, however the P-18 sample had a high conductivity. There is much yet to learn about structure and proton transport in these ionomer materials.

Conclusions and Future Directions

Model compound studies indicate that FPA protogenic groups show excellent promise for achieving high proton conduction rates in ionomers under conditions of low water availability. Proton hopping is demonstrated in the FPA acids but not in any other model acids. Ionomers prepared to date have not shown high conductivity, though conductivities have

steadily improved throughout the project term. Further refinement of synthesis procedures would undoubtedly bring about further improvements in conductivity, as would a focus on lower equivalent weight materials. Were the project to continue, these would be the directions it would follow. In addition, studies would be pursued on terpolymers having FPA groups combined with other acids, e.g. fluoroalkyl-sulfonic and -sulfonimide acids. These combinations might offer a possibility of proton hopping via protonated FPA groups, and also controlled crosslinking of low-equivalent weight ionomers via small amounts of FPA groups. The later approach could enable stabilization of low-equivalent-weight ionomers that would otherwise be water soluble, but which could have very high ionic conductivity.

FY 2009 Publications/Presentations

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2. O. Borodin, Q. Liu, B. Hopkins, G. Voth, M. Herath, D. DesMarteau, S. Creager, L. Jin, A. Kitaygorodskiy “Molecular Dynamics Simulations and Experimental Studies of Fluoroalkylphosphonic Acids” Advances in Polymer Electrolyte Membrane Fuel Cell Systems 2009, Feb. 15–18, 2009 Asilomar Conference Grounds, Pacific Grove, CA.
3. Stephen E. Creager, Darryl D. DesMarteau, Oleg Borodin, “Fluoroalkylphosphonic Acid Proton Conductors”, Presentation to Tech Team, Detroit, MI, January 2009.

4. Stephen E. Creager, Darryl D. DesMarteau, Oleg Borodin, "Fluoroalkylphosphonic Acid Proton Conductors", Presentation to DOE staff, Washington, D.C., February 2009.
5. Stephen E. Creager, Darryl D. DesMarteau, Mahesha Herath, Limei Jin, Arno Rettenbacher, Iqbal Sharif, Bing Liu "Proton-conducting fluoroalkylphosphonic and phosphinic acid electrolyte membranes for electrochemical energy conversion", Fluoropolymers 2008 conference, Charleston, SC, October 2008.
6. Stephen E. Creager, Darryl D. DesMarteau, Mahesha Herath, Limei Jin, Arno Rettenbacher, Iqbal Sharif, Bing Liu, "Proton-conducting electrolyte membranes for electrochemical energy conversion," Membranes Gordon Research Conference, New London, NH, August 2008.
7. Mahesha B. Herath, Alex Kitaygorodskiy, Stephen E. Creager, Darryl D. DesMarteau, "Proton Conductivity and PFG NMR Diffusion Studies in Perfluorinated Phosphonic Acid Based Systems" Poster presentation at Pittsburgh Conference, March 2009.

V.D.8 Poly(p-Phenylene Sulfonic Acids): PEMs with Frozen-In Free Volume

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Contract Number: DE-FC36-06GO16039

Project Start Date: March 1, 2006
Project End Date: February 28, 2011

Objectives

The project objectives are to optimize routes to rigid rod poly (phenylene sulfonic acids), develop methods to make them water insoluble, cast dimensionally stable films and characterize them as polymer electrolyte membranes (PEMs). This requires:

- Studying the parameters in the Ullman polymerization reaction necessary to get high molecular weight polymers.
- Increase the polymer sulfonic acid density by using phenylene disulfonic acid monomers.
- Develop reliable methods for making water-insoluble, dimensionally-stable PEMs by: 1) grafting non polar groups on the backbone, or 2), synthesizing water-insoluble comonomers that copolymerize well with the base monomers.
- Perform basic characterization of copolymers to understand the relationship between molecular structure, supermolecular organization and PEM properties.
- Submit the most successful materials for intensive testing.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research Development and Demonstration Plan.

- (A) Durability
- (B) Cost
- (C) Performance

Technical Targets

See Table 1.

Accomplishments

- The factors needed to get the highest molecular weight polymer possible using Ullman coupling have been determined. They are complete removal of oxygen and water. Polymerizations now take about 12 hours instead of ~150 hours. Molecular weight is limited by crystallization of the polymer from solution. Copolymers of the two base sulfonic acid monomers are more soluble and reach higher molecular weight than either homopolymer.
- Water uptake and conductivity as a function of relative humidity (RH) has been studied. The newest polymer, poly (phenylene disulfonic acid) (PPDSA), has a λ of 4.3 at 15% RH. The homopolymer has a large frozen-in free volume. It had high conductivity at very low relative humidity, ~100 mS/cm at 50% RH (25°C), and at 15% RH (75°C). It may meet the DOE 2015 requirements.
- One way of making water-insoluble, dimensionally-stable PEMs is to graft non-polar moieties on some of the sulfonic acid groups. Neopentyl benzene was grafted on poly(biphenylene disulfonic acid) (PBPDSA). A 4 mole% graft was water insoluble: a cast film was sent to Bekktech for testing. Conductivity at 50% RH was 115 mS/cm (80°C) and 150 mS/cm (120°C). Conductivity dropped drastically at lower humidities but was always above that of Nafion® 212. A neopentyl benzene graft (15 mole%) on PPDSA was tested in house. Conductivity at 30 and 80°C was equal to or greater than that of the earlier grafted polymer, especially at lower humidities, though lower than that of the homopolymer.
- Water absorption and “frozen-in free volume” was studied quantitatively. PBPDSA λ is greater by about 1.2 and PPDSA λ is greater by about 2.5 water

TABLE 1. Technical Targets: Membranes for Transportation Applications

Characteristic	Units	2005 Status ^a	2010	2015
Inlet water vapor partial pressure	kPa	50	<1.5	<1.5
Oxygen cross-over ^b	mA/cm ²	5	2	2
Hydrogen cross-over ^b	mA/cm ²	5	2	2
Membrane conductivity at inlet water vapor partial pressure and: Operating temperature 20°C -20°C	Siemens/cm Siemens/cm Siemens/cm	0.10 0.07 0.01	0.10 0.07 0.01	0.10 0.07 0.01
Operating temperature	°C	<80	≤120	≤120
Area specific resistance	Ohm - cm ²	0.03	0.02	0.02
Cost ^c	\$/m ²	25 ^d	20	20
Durability with cycling At operating temperature of ≤80°C At operating temperature of >80°C	hours hours	~2,000 ^e not applicable	5,000 ^f 2,000	5,000 ^f 5,000 ^f
Unassisted start from low temperature	°C	-20	-40	-40
Thermal cyclability in presence of condensed water		Yes	Yes	Yes

^a First year for which status was available.^b Tested in membrane electrode assembly (MEA) at 1 atm O₂ or H₂ at nominal stack operating temperature.^c Based on 2002 dollars and costs projected to high-volume production (500,000 stacks per year).^d Based on 2005 TIA study and will be periodically updated.^e Steady-state durability is 25,000 hours.^f Includes typical driving cycles.

molecules per sulfonic acid than Nafion® 117 from 15 to 75% RH. The “frozen-in free volume” for PPDSA was analyzed by comparing the volumes and inter-chain distance spacings (from X-ray scans) as a function of λ . The analysis showed a “frozen-in free volume” of 63 cc per sulfonic acid, a λ of 3.5, and a polymer van der Waals volume of 59 cc (the volume occupied by one half of a phenylene disulfonic acid in dilute solution). This was written up as a paper and is being published in an American Chemical Society (ACS) symposium volume (Andrew Herring, editor) of the 2008 Fuel Chemistry presentations.

Introduction

There are many problems associated with the use of aromatic polysulfonic acids derived from benzophenone, or the corresponding sulfone, ethers as PEMs. High sulfonation (ion exchange capacity [IEC] > 2.6 meq/gm) produces water soluble polymers. Water insoluble material with good conductivity swells greatly at high RH and loses conductivity rapidly as humidity drops [1]. Dimensionally stable polymers have a relatively low IEC and are not highly conductive except when wet. Recent approaches to overcome some of these problems use block copolymers where the dimensional stability is generated by a non-polar block and the

conducting block can have maximum sulfonation [2]. Block polymers still lose conductivity rapidly as RH decreases. Modeling suggests that the problem is due to the polyelectrolyte backbone structure. It is jointed and can collapse, losing volume easily by rotation around the ether links as humidity decreases. Conductivity drops rapidly with water loss. A possible solution is to design structures that cannot collapse as humidity is lowered. These could retain water at low humidities and therefore maintain conductivity even at elevated temperatures.

Approach

Our approach derives from a combination of polymer structure analysis and cost considerations. What type of polymer backbone can have high sulfonic acid content, hold water strongly, and yet have dimensional stability. The analysis suggested that poly (p-phenylene sulfonic acids), rigid rod liquid crystals that organize with all molecules locally parallel, should be suitable. These structures have small cross-section backbones with projecting sulfonic acid groups. Absorbed water separates the chains. As water is lost at low humidity, the sulfonic acids hit other acid groups or a neighboring polymer backbone. The system still has voids which can hold water (frozen in free volume): further compression distorts bond angles and requires high energy. As water is added, this structure can only expand perpendicular to the parallel polymer axes. It can be dimensionally stabilized by addition of non-polar groups that promote

hydrophobic bonding, or by cross-linking [3]. Non-polar groups that protrude further from the backbone than the acid groups can be incorporated; this increases the minimum chain (rigid rod) separation and thus increases the frozen-in free volume [4]. Such structures have non-collapsible nanopores lined with a high density of sulfonic acid groups. These hold water very strongly, both through H-bonding and capillary attraction.

Results

Early Results:

- The first polyelectrolytes tested (PBPDSA) passed the 2005 goals for membrane conductivity.
- Measurements of gaseous MeOH permeability (<0.04 mA/cm² for a 20- μ thick film at 100°C with a 2/1 MeOH/H₂O input) imply that the very polar membrane environment should reduce oxygen and hydrogen cross-over to values much lower than the target values.
- The graft copolymers had high dimensional stability, e. g. 27% expansion (z direction only) from 22 to 100% RH while retaining good conductivity.

Polymer Synthesis. Monomer synthesis is simple and straightforward – one step from cheap commercial materials, p-dibromo benzene or 4, 4'-dibromo biphenyl and fuming sulfuric acid, to the monomers, p-dibromo phenylene 2, 5-disulfonic acid, and 4, 4'-dibromo biphenyl 3, 3' disulfonic acid. Yields are ~ 80% for the biphenyl monomer and ~ 40% for the phenyl monomer. (We think that this can be ultimately raised to ~80% and are working on this now.) The polymerization route chosen was the Ullman reaction, coupling of halogen substituted aromatic compounds using copper metal to remove the halogens. While the reaction is well known, this is the first time it was used to make polymers with completely aromatic backbones. It was found that water retards the polymerization very strongly. When the reactants were dried at 120°C under high vacuum for one to two days, polymerization time at 140°C decreased from nine days to 12 hours and polymer was obtained with higher molecular weight than any made earlier. The ¹H nuclear magnetic resonance spectra are clean, showing only the major peaks and peaks due to the terminal bromophenyl groups. Integration showed a degree of polymerization of 35 to 40 (molecular weight [MWt] ~ 10,000 Daltons) for PBPDSA and 250 to 400 for PPDSA (MWt ~ 30,000 to 50,000 Daltons). Polymerization stopped when the polymer precipitated (probably crystallized). Further heating at 170°C for one and two days did not increase the viscosity.

The phenyl and biphenyl monomers copolymerized easily. There was some precipitation after 18 hours but the polymerization solution remained viscous.

The copolymer held water very strongly. The specific viscosity at 0.5% concentration was 1.5 dL/gm, much higher than the best of the homopolymers.

Recent studies on scaling up PPDSA homopolymerization showed that the present drying technique is difficult to use for larger batches. Viscosity of 0.5% solutions dropped as batch size increased, from 0.8 dL/gm (2 gm scale) to 0.6 to 0.7 (17 gm scale) to 0.25 (30 gm scale).

Copolymerization. Many potential comonomers were made by reacting the base monomer sulfonic acid groups to generate sulfones or sulfonates. None copolymerized effectively. Bis phenol sodium salts were also used in attempts to place non-polar groups on the backbone. Again, there was no effective reaction.

We have shifted the approach towards the synthesis of co-monomers that have long non-polar groups attached and have end groups that are direct analogues of the base monomers. This has worked, but the copolymer made was water soluble even at 33% substitution [3]. It had biphenyl substituents. We have since learned that long alkyl chains are necessary to get water insolubility at low degrees of substitution.

Graft Copolymers. Recent work has used neopentyl benzene (NPB) as the non-polar grafting moiety. We use polyphosphoric acid (PPA) as both solvent and condensing agent; the neopentyl group is not affected under the polymerization conditions. When NPB was grafted on to PBPDSA (4 mole%), a lightly crosslinked non water swelling polymer was obtained. This could be cast to make stable films with reasonable mechanical properties. They were stable at 100% RH, but disintegrated slowly when placed in water. A sample was sent to Bekktech for evaluation, which passed the DOE Go/No-Go requirements. The results are shown in Figure 1.

FIGURE 1. Conductivity of PBPDSA graft polymer (4 mole% NPB), Bekktech RDM-03, as a function of temperature and RH.

NPB was also grafted on PPDSA. A sample with 15 mole% substitution was cast and the film was tested in house; it had poor mechanical properties and was just water soluble. However, at low RHs its conductivity was better than that of the PBPDSA graft, Figure 2. PPDSA as the backbone polymer has advantages over PBPDSA; it has a higher IEC, holds water much better at low humidity and can have a higher molecular weight.

Water Absorption and “Frozen-In Free Volume”.

The water uptake of the two homopolymers has been reevaluated and correlated with their structures. Water uptake of PPDSA as a function of RH was compared to that for PBPDSA and Nafion® 117, Figure 3. (See

FIGURE 2. Comparison of PPDSA 15% NPB graft (25 and 80°C) and Bekktech RDM-03 (30 and 80°C): conductivities as a function of temperature and RH.

FIGURE 3. Comparison of lambda as a function of RH (25°C) for PPDSA, PBPDSA and Nafion® 117. Nafion® 117 λ is from least squares minimization of most literature values [6]. ($\lambda = 1.358 \times 10^{-5} (\%RH)^3 - 1.297 \times 10^{-3} (\%RH)^2 + 0.09105 (\%RH) + 1.067$)

reference 6 for the papers used to generate a least squares equation for Nafion® λ as a function of RH.) Even after extensive drying at 80°C under vacuum, the polymers retained one water molecule per acid group. (Nafion® holds one water molecule per acid group very strongly.) Both homopolymers absorb water strongly at low humidity, compared to Nafion®. PPDSA at 15% RH has a λ of 4.3. Nafion® reaches this value at ~75% RH.

The major driving force for water absorption in the polymer is its frozen-in free volume. The molar volume of PPDSA as a function of water absorption was modeled, see Equations 1 and 2 in the Figure 4 caption. The assumption is that water is initially absorbed in the frozen-in free volume. As this fills, water starts separating the chains, increasing the polymer volume. Two PPDSA data sets were used: 1) polymer molar volumes were measured, and 2) the wide-angle X-ray diffraction (WAXD) low angle peaks, the chain separation d spacings, were measured for two film orientations at each RH. The measured volumes correlated linearly with d², showing that water absorption caused the chain separation to increase isotropically. The equations developed correlated both the measured molar volume and that calculated from the d spacings, Figure 4. The calculated “frozen-in free volume” was 63 cc/sulfonic acid, equivalent to a λ of 3.5 [5].

The important factors governing conductivity of sulfonic acid polymers seem to be λ and temperature; RH affects λ, but the polymer structure determines its value. The high conductivity of our materials at low

FIGURE 4. Determination of “frozen-in free volume” using Equation 1. Data for λ = 1.2 not used. WAXD scans taken through films. d(1) perpendicular to casting direction; d(2) parallel to casting direction.

1. $MV = VdWV + 18\lambda + FV * (1 - \tanh(18\lambda / FV))$
2. $1.27d^2 = K * MV$

MV = Molar Volume measured, per SO₃H group

VdWV = Polymer Van der Waals Molar Volume

FV = “Frozen-In Free Volume” per SO₃H group

K = Macro to molecular volume conversion coefficient

RH demonstrates this very well. PPDSA conductivity at 75°C and 15% RH was almost 100 mS/cm. Since water is held very strongly, that generated by the fuel cell operation could be enough to maintain high conductivity above 100°C.

Conclusions and Future Directions

- Polymerization conditions for the Ullman reaction have been optimized. The limiting factor for getting high molecular weight polymer is polymer precipitation (crystallization) from solution. Copolymerization of the two base monomers avoids this; higher viscosity polymer was obtained.
- The existence of frozen-in free volume and its importance for retaining high conductivity at low relative humidity has been demonstrated. Incorporating non-polar alkyl substituents should make the polymer water insoluble, imparting dimensional stability while maintaining low humidity conductivity.
- The homopolymers are water soluble. Grafting of non-polar groups on the backbone occurs under heterogeneous conditions and is difficult to control. Water-insoluble, dimensionally-stable, highly-conductive PEMs were made earlier using this method, but control of grafting and scaling up is very difficult. A new graft copolymer film from PBPDSA (4 mole% NPB) was made and sent to Bekktech for evaluation. Conductivity at 50% RH was above 100 mS/cm at both 80 and 120°C. PPDSA was grafted (15 mole% NPB) and conductivity was measured in house. Values at lower humidities were much higher than those measured for the PBPDSA graft.
- The major remaining synthetic challenge is to make high molecular weight water insoluble copolymer. Work has started on some new approaches. First, the Suzuki reaction can be used to make a comonomer that has a central non-polar substituent and end groups that are identical with those of the base monomer. This was done earlier and good copolymers were obtained, but the group chosen, biphenylene, gave water-soluble polymer even at 33 mole% substitution; it was not hydrophobic enough [3]. All work so far demonstrates that comonomers with long alkyl chains are necessary to confer dimensional stability.
- Once water insoluble polymers are made, the next challenge is to develop reasonable mechanical properties. Copolymerization of a non-polar comonomer with both base monomers might do this. The irregular arrangement of the groups in the backbone should keep the chains from crystallizing and we should be able to reach higher molecular weights than we are now getting. That, plus the hydrophobic interactions of the non-polar groups

should produce dimensionally-stable polymers with reasonable elongation. Dimensionally-stable PEMs, even with relatively poor mechanical properties, will be submitted for further evaluation.

- Work to understand the structure/property relationships in these systems will continue.

Special Recognitions & Awards/Patents Issued

1. The August 2008 Fuel Chemistry Division symposium on fuel cells has generated a Symposium volume (editor, Andrew Herring) that includes a paper based on my presentation. It will be published soon.

FY 2009 Presentations

1. 1/14/09 USCAR presentation, Greenfield, MI.
2. 5/19/09 DoE annual review, Washington, D.C.
3. 8/15/09 ACS Fuel Chemistry Division Symposium.

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V.D.9 NanoCapillary Network Proton Conducting Membranes for High Temperature Hydrogen/Air Fuel Cells

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Contract Number: DE-FG36-06GO16030

Subcontractor:
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Start Date: March 1, 2006
Projected End Date: February 28, 2011

Objectives

- Fabricate a new class of nanocapillary network (NCN) proton conducting membranes using different sulfonated polymers.
- Add sulfonated molecular silica to the polymers prior to fiber spinning.
- Characterize the membranes in terms of swelling, proton conductivity, thermal/mechanical stability, and gas permeability.
- Optimize the membrane structure (fiber diameter, mat density, polymer ion-exchange capacity, choice of impregnation polymer, etc.) to achieve the DOE proton conductivity target.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) Durability
- (B) Cost
- (C) Performance

Technical Targets

This project is focused on the fabrication and characterization of a new class of proton conducting membranes for high temperature hydrogen/air fuel cells. The technical targets of this project are listed in Table 1 in terms of a Year 2 (3rd quarter) milestone and a Year 3 (3rd quarter) Go/No-Go target.

Accomplishments

- Developed a method for electrospinning nanofiber mats composed of perfluorosulfonic acid (PFSA) polymer, where the PFSA polymer was co-spun with a small amount of high molecular weight (MW) poly(ethylene oxide) (PEO) or poly(acrylic acid) (PAA).
- Fabricated mats from 1100 equivalent weight (EW) Nafion[®] and from low EW 3M Corp. PFSA polymers (733 EW and 825 EW).
- Fabricated PFSA nanofiber mats with an average fiber diameter in the range of 200 nm–6 μ m.
- Developed procedures for converting electrospun PFSA mats into nanofiber network composite membranes (polymer annealing and interfiber welding, mat compaction, and embedding with inert polymer).
- Performed preliminary membrane characterization experiments (proton conductivity as a function of temperature and relative humidity [RH] and mechanical property tests).
- Prepared impregnated nanofiber membranes where the nanofibers were composed of 825 EW PFSA polymer (from 3M Corp.) with sulfonated octaphenyl polyhedral oligomeric silsesquioxanes (sPOSS) from Michigan Molecular Institute.
- Determined the proton conductivity of membranes containing 825 EW PFSA + sPOSS and sent samples out for independent conductivity testing.

TABLE 1. Progress towards Meeting Technical Targets for Membranes for Transportation Applications

Characteristic	Units	2007 DOE Milestone (Year 2, 3Q)	2010/2015 DOE Target (Year 3, 3Q)	2007 Status for NCN Membranes	2008 Status for NCN Membranes
Inlet water vapor pressure	kPa	50	<1.5	50	<1.5
Oxygen cross-over	mA/cm ²	5	2	0.01 ¹	
Hydrogen cross-over	mA/cm ²	5	2		
Membrane Conductivity at inlet water vapor partial pressure Operating Temp 20°C -20°C	S/cm S/cm S/cm	0.10 0.07 ¹ 0.01	0.10 0.07 0.01	0.072 ²	0.107 ³
Operating temperature	°C	<80	≤120	30	120
Area specific resistance	Ohm-cm ²	0.03	0.02	0.069	0.10
Durability with Cycling At operating T <80°C At operating T >80°C	hours hours	~2,000	5,000 2,000 (5,000 for 2015)		

¹ at 25°C and 50% relative humidity (RH)² Proton conductivity at 30°C and 80% RH – data from Bekktech LLC³ Proton conductivity at 120°C and 50% RH – data from Bekktech LLC

- The proton conductivity of a nanofiber membrane with 825 EW PFSA + sPOSS met the DOE 2008 Go/No-Go target of 0.10 S/cm at 120°C and 50% RH.

Introduction

Proton exchange membrane (PEM) hydrogen/air fuel cell operation with lightly humidified gases at 120°C would be highly advantageous with regards to heat rejection from a fuel cell stack, compatibility with automotive radiators, tolerance to CO impurities in the hydrogen gas stream, and faster electrode kinetics. For PEM fuel cell operation at T ≤ 80°C and high RH conditions, PFSA proton conductors (e.g., Nafion®) are the membrane material of choice due to their high conductivity and chemical/mechanical stability [1]. Unfortunately, the conductivity of PFSA membranes drops dramatically at T > 100°C under low humidity conditions [2] due to an insufficient number of membrane-phase water molecules for protons to dissociate from sulfonic acid sites, a loss of percolation pathways for proton movement, and structural changes in the polymer which cause membrane pores to collapse.

In order to overcome the limitations of existing membrane materials, a new approach to fuel cell membrane design and fabrication is being developed, where a three-dimensional interconnected network of proton-conducting polymer nanofibers/nanocapillaries is embedded in an inert/impermeable polymer matrix. The nanocapillary network is composed of a high ion-exchange capacity sulfonic acid polymer to ensure high

water affinity and a high concentration of protogenic sites. The inert (hydrophobic) polymer matrix controls water swelling of the nanofibers/nanocapillaries and provides overall mechanical strength to the membrane. First generation membranes were created using sulfonated poly(arylene ether sulfone) (sPEAS) for the nanofibers with sPOSS to further boost the conductivity and Norland Optical Adhesive 63 (NOA 63) as the inert embedding polymer [3]. The resulting membrane had a proton conductivity of 72 mS/cm at 30°C and 80% RH (measured by Bekktech), which met the 2007 DOE target. These membranes, however, did not meet the Year 3, 3rd quarter conductivity goal of 100 mS/cm at 120°C and 50% RH. Consequently, sPAES was replaced by a low EW PFSA polymer.

Approach

To achieve the Go/No-Go target conductivity, NCN membranes were prepared with electrospun nanofibers composed of PFSA, as a replacement for sPAES. 1100 EW Nafion® and low EW (733 and 825 EW) 3M Corp. PFSA polymers were examined. Nanofiber mats were also prepared from a mixture of 825 EW polymer with sPOSS (25 and 35 wt%). After electrospinning, the mats were processed into ion-exchange membranes by: (i) annealing the fibers at 140°C for 5 minutes (during annealing, intersecting fibers were welded to one another to create a 3-dimensional fiber network), (ii) compacting the mats (at 10,000 psi for five seconds) to increase the fiber volume fraction to 0.70-0.75, and (iii) imbibing an inert polymer, NOA 63, into the mats. The resulting membranes were evaluated by measuring in-plane proton conductivity as a function of temperature and RH.

Results

Preparing Electrospun Mats with PFSA Polymer

– PFSA polymer with an EW of 825 was electrospun, yielding high quality nanofiber mats of uniform thickness and fiber volume fraction. Electrospinning was accomplished by adding a small amount of a high molecular weight, water soluble polymer to the spinning solution, either PEO or PAA. Fibers were electrospun with a very small amount of the dopant polymer, either 0.3 wt% PEO (10⁶ MW) or 5 wt% PAA (450,000 MW), where the total polymer concentration in the electrospinning solution was 15 wt% and the electrospinning solvent was a 1-propanol/water mixture (2:1 weight ratio). For PFSA/PEO mats, the electrospinning conditions were 3 kV potential, 6 cm spinneret-to-collector distance, and 0.50 mL/h polymer solution flow rate. Scanning electron microscope (SEM) surface images of electrospun 825 EW PFSA mats are shown in Figure 1, for three different PEO dopant concentrations. An undesirable bead-on-fiber morphology was produced when the PEO concentration was decreased to 0.2 wt%. 825 EW PFSA was also cospun with PAA, with and without sPOSS. SEM images of the resulting nanofiber mats are shown in Figure 2, where the PFSA/sPOSS/PAA mat had a fiber composition of 60 wt% PFSA + 35 wt% sPOSS + 5 wt% PAA, an average fiber diameter of 247 nm, and a fiber volume fraction of 0.21.

Nanofiber Network Membrane Preparation -

PFSA/PEO, PFSA/PAA, and PFSA/sPOSS/PAA nanofiber mats were first annealed at 140°C for 5 minutes. During annealing, intersecting fibers were welded to one another (see Figure 3). After annealing, there was a modest increase in the volume fraction of fibers in the mat (from about 0.20 to about 0.30). The annealed/welded mat was compacted further at 10,000 psi for 5 seconds to increase the fiber volume to 0.70-0.75. NOA 63 was then impregnated into the mat by immersion in liquid NOA with degassing under vacuum at 50°C for 30 minutes, removing the mat from the liquid and wiping excess NOA 63 from the mat surface, and exposing the mat to UV light (1 hour each side) in a nitrogen atmosphere. The final membranes had a dry thickness of approximately 100 µm.

Proton Conductivity of PFSA/sPOSS Nanofiber Network Membranes – In-plane proton conductivities of nanofiber network membranes were collected on a sample film 104 µm in thickness, where the nanofiber mat was composted of 60% 825 EW PFSA + 35 wt% sPOSS + 5 wt% PAA and the volume fraction of nanofibers was 0.74. Samples were tested in-house at 30°C and 80°C and duplicate membranes were sent to the University of Central Florida for independent conductivity measurements by Bekktech LLC (at 30°C, 80°C, and 120°C). The results are shown in Figure 4, where conductivity is plotted against RH for three

FIGURE 1. SEM surface images of nanofiber mats, made by cospinning 825 EW PFSA (from 3M Corp.) with 10⁶ MW PEO (3,000x magnification). The PFSA/PEO weight ratio in the spinning solution is listed above each micrograph.

different temperatures. As can be seen, the proton conductivity of the nanofiber membrane was very high and met (slightly exceeded) the DOE Go/No-Go target of 100 mS/cm at 120°C and 50% RH.

Conclusions and Future Directions

Conclusions

- Electrospun nanofiber mats were fabricated from low EW, high ion exchange capacity PFSA polymer

FIGURE 2. SEM surface images of nanofiber mats (10,000x magnification). Top: Nanofibers composed of 95 wt% PFSA (825 EW) + 5 wt% PAA. Bottom: Nanofibers composed of 60 wt% PFSA (825 EW) + 35 wt% sPOSS + 5 wt% PAA.

(825 EW PFSA, supplied by 3M Corporation). The fiber volume fraction of as-spun mats was approximately 0.20.

- Well-formed nanofiber mats (with no beads and droplets) were made by adding a high MW polymer dopant to the PFSA electrospinning solution, at a very low concentration. PEO and PAA were used successfully as dopants during electrospinning, at a minimum concentration of 0.3 wt% and 5 wt%, respectively (wt% is relative to the weight of PFSA).
- Welding of PFSA nanofibers occurred during polymer annealing, thus simplifying the mat processing steps.
- Mechanical compaction of PFSA mats (10,000 psi for 5 seconds) was used to increase the fiber volume fraction from 0.20-0.30 to 0.70-0.75.
- The inter-fiber voids were filled with NOA 63, followed by ultraviolet light curing.
- Electrospun fiber mats were produced from blends of 825 EW PFSA (from 3M Corp.) and sPOSS, purchased from Michigan Molecular Institute. The fiber volume fraction of an as-spun mat

FIGURE 3. SEM images (10,000x magnification) of nanofiber mats before and after annealing (annealing conditions: 140°C for 5 min). Fiber composition: 95 wt% PFSA (825 EW) + 5 wt% PEO.

FIGURE 4. Proton conductivity vs. RH of nanocapillary composite membranes. Nanofiber mat was composed of 60 wt% PFSA (825 EW) + 35 wt% sPOSS + 5 wt% PAA. ● 120°C; ▼ 80°C; ■ 30°C.

was approximately 20%; and the average fiber diameter was in the 300-400 nm range. The final composition of the nanofibers was 60 wt% PFSA + 35 wt% sPOSS + 5 wt% PAA.

- The proton conductivity of the PFSA/sPOSS/PAA mats was 107 mS/cm at 120°C and 50% RH, which exceeded the DOE 2008 Go/No-Go target of 100 mS/cm.

Future Work

- Investigate possible leaching of sPOSS from the nanofiber membranes - Identify sPOSS leaching by a loss in proton conductivity after soaking membranes in liquid water; prepare sulfonated POSS with a lower ion exchange capacity to eliminate leaching.
- Replace sPOSS with sulfonated poly(phenylene) to boost conductivity - Sulfonated poly(phenylene) will have improved chemical stability as compared to sPOSS, with no dissolution in water; add up to 60% high ion exchange capacity (e.g., 7.0 mmol/g) sulfonated poly(phenylene) to PFSA nanofibers to increase proton conductivity at low RH.
- Replace NOA 63 as the inert matrix polymer - Perform multiple embedding steps with a polymer/solvent solution (with solvent evaporation between repeated embedding steps); examine polysulfone Radel R, polyvinylidene fluoride, and polyvinylidene fluoride/hexafluoropropylene copolymers (Kynar Flex) as the inert matrix material; add inorganic particles e.g., organically modified aluminosilicate (clay) or glass fibers to the embedding polymer for improved strength.
- Further characterize nanofiber membranes - Measure mechanical properties, gas permeability, and water vapor uptake as a function of temperature and RH.
- Prepare and test hydrogen/air fuel cell membrane electrode assemblies with nanocapillary network membranes.
- Examine different fiber morphologies with PFSA polymers (hollow bore nanocapillaries, core shell nanofibers, etc.).

Patents Issued

1. P.N. Pintauro, P. Mather, and R. Wycisk, "Fiber Network Membrane," U.S. Provisional Patent (2008).

FY 2009 Publications/Presentations

1. Jonghyun Choi, Kyung Min Lee, Ryszard Wycisk, Peter N. Pintauro, and Patrick T. Mather, "Composite Nanofiber Network Membranes for PEM Fuel Cells," in Proton Exchange Membrane Fuel Cells 8, *Electrochemical Society Transactions*, **16(2)** 1433 (2008).

2. Jonghyun Choi, Kyung Min Lee, Ryszard Wycisk, Peter N. Pintauro, and Patrick T. Mather, "Composite Nanofiber Network Membranes for PEM Fuel Cells," presentation given at the 2008 Fall Electrochemical Society Meeting, October 2008, Honolulu, HI.

3. Jonghyun Choi, Kyung Min Lee, Ryszard Wycisk, Peter N. Pintauro, and Patrick T. Mather, "Nanofiber Network Membranes for Fuel Cell Applications," presentation given at the Annual Meeting of the American Institute of Chemical Engineers, November 2008, Philadelphia, PA.

4. Peter N. Pintauro, "New Fuel Cell Membranes via Nanomorphology Manipulation" seminar given at Clarkson University, Department of Chemical and Biomolecular Engineering, Potsdam, NY, October 2008.

5. Peter N. Pintauro, "New Fuel Cell Membranes via Nanomorphology Manipulation" seminar given at the University of Kentucky, Department of Chemical Engineering, Lexington, KY, October 2008.

6. Peter N. Pintauro, "New Membrane Nano-morphologies for Improved Fuel Cell Operation" seminar given at Georgia Tech, Department of Chemical Engineering, Atlanta, GA, February 2009.

7. Peter N. Pintauro, "Composite Nanofiber Network Membranes For PEM Fuel Cells" presentation at Nissan Technical Center, North America, Farmington Hills, MI, March 2009.

8. Jonghyun Choi, Peter N. Pintauro, Kyung Min Lee, Ryszard Wycisk, and Patrick Mather, "Nanofiber Network Ion-Exchange Membranes for PEM Fuel Cells" presentation at the American Chemical Society Spring National Meeting, Salt Lake City, Utah, March 2009.

9. Peter n. Pintauro, "NanoCapillary Network Proton Conducting Membranes for High Temperature Hydrogen/Air Fuel Cells" presentation at USCAR, Southfield, MI, March 2009.

10. Peter N. Pintauro, "New Membrane Nano-morphologies for Improved Fuel Cell Operation" seminar given at University of Louisville, Department of Chemical Engineering, April 2009.

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V.D.10 High Temperature Membrane with Humidification-Independent Cluster Structure

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Contract Number: DE-FG36-06GO16033

Start Date: June 1, 2006

Projected End Date: May 31, 2011

Technical Targets

This project is developing a composite membrane to meet the following DOE 2010 technical targets for membranes:

- Membrane Conductivity: At $\leq 120^{\circ}\text{C}$: 0.1 S/cm; at room temperature: 0.07 S/cm; at -20°C : 0.01 S/cm.
- Cell Area Specific Resistance: $0.02\ \Omega\text{cm}^2$.

Accomplishments

- Prepared three batches of improved co-polymer, with successively lower equivalent weight.
- Fabricated and characterized six additive batches for water retention and protonic conductivity enhancement.
- Developed a new solvent system for improved additive dispersion and casting.
- Synthesized over ten batches of multi-component composite (mC^2) membrane.
- Measured conductivity of more than 25 membrane samples, including 12 samples verified by BakkTech.
- Met the DOE 120°C conductivity goal of 0.1 S/cm at 50% relative humidity (RH).
- Demonstrated $>2\times$ improved conductivity at 120°C over 2008 ($\sim 3\times$ higher than NRE-212[®]).
- Met all program milestones for the year.

Objectives

Develop humidity-independent, thermally stable, low equivalent weight composite membranes with controlled ion-cluster morphology, to provide high proton conductivity at up to 120°C (overall goal: meet DOE 2010 targets).

- Improve mechanical properties to significantly increase the durability and reduce the gas cross-over.
- Expand the operating range to sub-freezing temperatures.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section (3.4) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) Durability
- (B) Cost
- (C) Performance

Introduction

This project is focused on the development of composite proton exchange membranes that can operate at low RH and over a wide temperature range (-20 to 120°C). The goal is to develop a structure in which ion conducting clusters remain intact at low RH. A major challenge is that current proton conducting polymers cannot sufficiently hold on to water under these conditions. Since the conduction mechanism relies on movement of hydrated species, the conducting path is compromised, resulting in low performance. Membranes that can operate at lower RH at elevated temperatures up to 120°C will reduce the fuel cell system complexity and cost. This project is developing a composite membrane, in which both the ionic conductivity and mechanical properties are enhanced to meet DOE's ambitious goals for transportation fuel cells.

Approach

The approach to address each of the DOE target parameters is summarized in Table 1. The 120°C conductivity target is the Fiscal Year 2009 Go/No-Go milestone and is therefore highlighted in the table.

TABLE 1. Approach for the Composite Membrane

Target Parameter	DOE Target (2010)	Approach
Conductivity at: $\leq 120^{\circ}\text{C}$	0.1 S/cm	Multi-component composite structure, lower equivalent weight
: Room Temp.	0.07 S/cm	Higher number of functional groups
: -20°C	0.01 S/cm	Stabilized nano-additives
Inlet water vapor partial pressure	1.5 kPa	Immobilized cluster structure
Hydrogen and oxygen cross-over at 1 atm	2 mA/cm ²	Stronger membrane structure; functionalized additives
Area specific resistance	0.02 Ωcm^2	Improved bonding capability for membrane electrode assembly
Cost	\$20/m ²	Simplified polymer processing
Durability: - with cycling at $>80^{\circ}\text{C}$ - with cycling at $<80^{\circ}\text{C}$	2,000 hours 5,000 hours	Thermo-mechanically compliant bonds, higher glass transition temperature
Unassisted start from low temp.	-40°C	Stabilized cluster structure design

Results

The main focus of this year's effort has been on increasing the proton conductivity at the Go/No-Go milestone conditions of 120°C and 50% RH. In-plane conductivity measurements at 120°C as a function of RH were carried out on the composite membranes. The results, shown in Figure 1, clearly demonstrate that the DOE target of 100 mS/cm at 50% RH has been met. The data show an improvement in conductivity over that of the improved polymer of ~50% when water retaining additive is added, and >130% when both additives are incorporated. The result is a conductivity of mC² of ~3x that of state-of-the-art Nafion® membrane (NRE-212®).

FCE's concept for the multi-component composite membrane, named mC², has been used in our design of more conductive membranes. The efforts were centered on improving each of the following mC² components:

- Co-polymer
- Water retention additive
- Protonic conductivity enhancer

FIGURE 1. Conductivity of improved polymer (M54) is significantly enhanced by incorporating water retaining additive (M60) and water retaining additive with protonic conductivity enhancer (M61).

The co-polymer provides the basic building block for the membrane. It is an advanced perfluorinated sulfonic acid with significantly higher conductivity than state-of-the-art polymers. The conductivity of the co-polymer was increased compared to FY 2008 by increasing the number of functional groups and by improving the polymer formulation. This resulted in a 50% increase in conductivity (measured at 120°C and 50% RH).

The functionalized additives are designed to retain water at the low RH conditions and to enhance the composite membrane's proton conductivity by providing an alternate proton conduction path [1]. This path is designed to efficiently transport protons at high temperature as well as subfreezing conditions. Additive development was focused on particle size reduction and improvements in the dispersion and uniformity of the composite membrane.

Development of a new synthesis process led to reproducible additive particle size <100 nm, as shown in Figure 2. The nature and morphology of the particles was studied by X-ray diffraction measurements, chemical analysis by inductively coupled plasma, surface area analysis and transmission electron microscopy [2]. Process modifications were developed to stabilize particle size during the processing of the additives into a composite membrane. Moreover, the interaction between the water retaining additive and the protonic conductivity enhancer was studied. The additives were modified to allow for immobilization of the protonic conductivity enhancer on the water retaining additive particles. This interaction strengthens the synergy between the additives and ensures stability during mC² fabrication and in the fuel cell environment.

FIGURE 2. Water retaining additive average particle size < 100 nm was achieved with a new synthesis process, as confirmed by dynamic light scattering.

Conclusions and Future Direction

A multi-component composite membrane design for high temperature and low RH operation has been successfully implemented to fabricate membranes with enhanced conductivity. A three times higher conductivity at 120°C compared to state-of-the-art Nafion® membrane has been demonstrated. In the next year we will continue the composite membrane development, with an emphasis on the following activities:

- Continue to develop advanced polymer dispersions.
- Optimize and further simplify integration of the additives.
- Measure progress towards DOE's conductivity and area specific resistance targets.
- Perform cell testing at 95°C and 120°C.
- Initiate membrane durability testing.
- Expand membrane characterization to track progress towards DOE 2015 targets.

FY 2009 Publications/Presentations

1. Presentation to the FreedomCAR Tech Team on March 18, 2009.
2. L. Lipp, "High Temperature Membrane With Humidification-Independent Cluster Structure", 2009 DOE Hydrogen Program and Vehicle Technologies Program Annual Merit Review and Peer Evaluation Meeting, Arlington, VA, May 18–22, 2009.

References

1. L. Lipp, "High Temperature Membrane With Humidification-Independent Cluster Structure", 2008 DOE Hydrogen Program Merit Review and Peer Evaluation Meeting, Washington D.C., June 11, 2008.
2. L. Lipp, "High Temperature Membrane With Humidification-Independent Cluster Structure", 2009 DOE Hydrogen Program and Vehicle Technologies Program Annual Merit Review and Peer Evaluation Meeting, Arlington, VA, May 18–22, 2009.

V.D.11 Novel Approaches to Immobilized Heteropoly Acid (HPA) Systems for High Temperature, Low Relative Humidity Polymer-Type Membranes

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Project Start Date: April 1, 2007
Project End Date: March 31, 2011

Objectives

- To develop a new class of proton exchange membranes (PEMs) using polymers based on heteropoly acid (HPA) functionalized with organic monomers (polyPOMs).
- To understand the mechanism of proton conduction in the polyPOMs and optimize it for proton conduction under low humidity, higher temperature fuel cell operating conditions.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

(A) Durability

(B) Cost

(C) Performance

Technical Targets

The materials have so far only been evaluated in terms of proton conductivity at various temperatures and relative humidity, Table 1.

TABLE 1. Progress towards Meeting Technical Targets for Membranes for Transportation Applications

Condition	80°C/100% RH	30°C/<80% RH	120°C/<50% RH
Target H ⁺ conductivity	100 mS cm ⁻¹	> 70 mS	100 mS cm ⁻¹
Date Met	April 2008	August 2008	January 2009
H ⁺ conductivity achieved	300 mS cm ⁻¹	126 ms cm ⁻¹	>100 ms cm ⁻¹

RH – relative humidity

Accomplishments

- Fabricated ionomer films based on HPAs with high loadings that have proton conductivities >0.1 S cm⁻¹ at >80°C and <50% RH. The results were verified independently by 3M and Scribner and Associates.
- Showed that proton conductivity was strongly correlated with chemistry, best performance was from films containing only HPA as the protogenic group.
- Also showed that process conditions strongly influenced morphology that affected all film properties. Ultraviolet (UV)-cured films were brittle, but had proton conductivities that made all targets shown above, whereas thermally cured films were much stronger but had poor proton conductivity.

Introduction

Currently, fuel cells based on perfluorosulfonic acid (PFSA) PEMs are limited to operating conditions of ≤80°C and very high inlet RHs, because proton conduction in these materials depends strongly on the presence of water. For automotive applications it is desirable to operate the fuel cell at a temperature of ≤120°C and low RH to enable the use of existing radiator technology and to eliminate the parasitic loads and system complications associated with

externally humidifying the gas streams. Displacement of internal combustion engines by PEM fuel cells would dramatically facilitate the adoption of the hydrogen economy and enable a smooth transition from fossil fuels to hydrogen produced solely from renewable sources. Materials suitable for use in automotive PEM fuel cells are being developed that have high proton conductivities, $>0.1 \text{ S cm}^{-1}$ at 80% RH operating temperatures of -30 to 120°C , low area specific resistance, $<0.1 \Omega\text{cm}^2$, suitable for incorporation in a fuel cell membrane electrode assembly. We anticipate that the use of HPAs will generate membranes with oxidative stabilities higher than observed for any PFSA ionomer to date.

Of all the inorganic proton conductors that have been exploited for fuel cell applications the HPA may have the greatest potential as they not only have high proton conductivities but they have significant synthetic versatility [1]. In previous work (DE-FC02-0CH11088) we have shown that the HPAs have very high proton conductivities at room temperature and can be operated at ambient conditions in a fuel cell using dry gases [2]. Importantly, we demonstrated that some of the protons in HPA have very impressive rates of proton diffusion at elevated temperatures, $>100^\circ\text{C}$ under dry conditions. The residual protons in these systems are immobile at elevated temperatures resulting, however, in rather low conductivities. The two key challenges that need to be addressed, therefore, are utilization of all protons under elevated temperature, dry conditions, and immobilization of the water soluble HPA in practical membranes for fuel cell use.

Approach

Our approach is to functionalize HPA with monomers so that they can be fabricated into polymeric materials with the use of a suitable co-monomer. We chose to use acrylates as the co-monomers in this project because this represents a polymer system in a kit leaving the synthetic effort to be devoted to making the HPA monomers. This polymer system allows the chemistry to be easily varied so that the effect of morphology can be studied. In addition as these are free radical polymerizations the materials are easily obtained as films from the polymerization of the cast solutions of co-monomers. We are the first research group to fabricate proton-conducting free-standing films of these materials, but as they have been previously synthesized as gels [3], we are able to fully disclose our research using this model system. However, the system has certain inherent disadvantages that include an acrylate

ester linkage that is unstable to hydrolysis, and polymers that contain readily oxidizable methylene groups and an oxidizing super acid moiety.

The team assembled includes inorganic and polymer chemists and chemical and materials engineers from both CSM and 3M. CSM and 3M fabricate the HPA monomers and the extensive knowledge of polymers at 3M is heavily exploited. The polymer system in this project is not restricted, but the mode of proton conduction is mediated by the HPA. In this year's work we have concentrated on making films with even higher HPA loadings, pushing the system to the limit. We have also used nuclear magnetic resonance (NMR) to measure the self diffusion coefficient of water and to quantify the amount of water. Comparing the NMR data with the proton conductivity data allows us to understand proton transport in these unique systems. In addition we are now correlating proton conductivity with morphology as observed by atomic force microscopy (AFM) and small angle X-ray scattering.

Results

Figure 1 shows the design space that was probed in this system and the eventual practical limit with the polyPOM acrylate approach that gives proton conductivities that exceed the DOE goals. The initial intent was to co-polymerize the HPA monomers with acrylates substituted with proton containing groups with various degrees of proton dissociation. HPA-co-hydroxyethyl acrylate polymers all had lower proton conductivities than HPA-co-butyl acrylate polymers, presumably as the HPA could not dramatically increase the dissociation of protons in the hydroxyl groups. We, therefore, concentrated on the butyl acrylate system as the other alternatives such as carboxylic acid, sulfonic acid and phosphonic acid substituted acrylates provided additional problems in increased solubility of the system

FIGURE 1. Design Space for PolyPOMs based on Acrylate Chemistry

and in the case of carboxylic acid decreased stability of the eventual PEM. The linkage was chosen to be Si as functionalized silanes are readily available commercially, again minimizing resource intensive synthetic efforts. We had a choice of free radical polymerizable groups with which to functionalize the HPA which included vinyl, methacrylate, styrenyl and ethylstyrenyl. The styrenyl monomers had solubility issues precluding their use in a solvent free system and the ethylstyrenyl silane was only available as a mixture of isomers which did not allow for complete characterization of the material. The methacrylate monomer produced films with interesting proton conducting properties but these materials had severe structural deficiencies at moderate temperatures. Only vinyl substituted monomers easily gave films with desirable properties.

It was found that the material needed to be ≥ 50 wt% HPA to achieve phase separation and high conductivity. A 75 wt% HPA material was found to have proton conductivity *ca.* 10% higher than for a standard sample of Nafion[®] 212 at 100% RH from 30 to 120°C [4,5]. However, the proton conductivity of the material below 70% RH rapidly dropped off, as is also typical for a number of hydrocarbon-based PEMs. As this was not a solution that would result in a PEM that could operate in a fuel cell without inlet humidification it was decided to increase the loading of the HPA monomer. A loading of 85 wt% of HPA monomer has so far proven to be the limit achievable in these films as considerable amounts of solvent are required at high HPA loadings resulting in films with poorer properties. Whereas the polymers with 75 wt% of HPA were well behaved and easily characterized, the materials with 80 and 85 wt% proved to have considerable variability in their properties. In Figure 2 we show the in-plane proton conductivities of a series of polyPOMs with HPA loadings varying

from 75 to 85 wt%, at 120°C and <50 % RH. The proton conductivities vary from 15 to 110 mS cm⁻¹. Both an 80 wt% and an 85 wt% sample had proton conductivities of *ca.* 100 mS cm⁻¹ at these conditions, this is significant because this represents a practical proton conductivity at an RH where inlet humidification would not be required in the fuel cell system. This result is very exciting, but we were frustrated by the fact that this result was hard to reproduce.

From observations that the film properties seemed to change with time when the films were left exposed to ambient conditions and that film properties could be enhanced by storing the films in a humid environment we decided to probe the effect of film morphology. Two extremes of curing conditions were chosen, UV curing with minimal solvent and thermal curing using solvent in an oven at 120°C for the same formulation of poly(SiW₁₁80wt%Vinyl-co-17.5wt%butyl acrylate-co-2.5wt%1,6-hexanedioldiacrylate). This resulted in two films of radically different properties. The thermally cured film appeared ductile and strong; whereas the UV-cured film was somewhat brittle. The micro structure of these two films is contrasted in Figure 3. It can be seen that the thermally cured film has a clustered morphology in both the environmental scanning electron microscope (ESEM) and AFM. The clusters are large *ca.* 500 nm. For the UV-cured film a network morphology is observed and AFM shows a striated morphology consistent with what would be imagined to be a brittle material.

Generally we observe high proton conductivities for the UV-cured films as opposed to the thermally-cured films, *e.g.* >80 mS cm⁻¹ and <20 mS cm⁻¹, respectively at 120°C and 50% RH. When we examine the self diffusion coefficients of these materials by pulsed field gradient spin (PFGSE) NMR, Table 2 shows some typical data, we see that diffusion of protons is restricted in both materials as it differs dramatically between short length scales $D(0)$ and its limit, $D(\infty)$ at long length scales. The self diffusion of protons in the thermally cured film seems to be much more severe on a qualitative basis than the UV-cured film as $D(0)$ is six times larger than $D(\infty)$ in the thermally cured films and only three times larger in the UV-cured film. However the diffusion coefficients are an order of magnitude lower for the thermally cured film at 120°C and 50% RH. When we combine the diffusion coefficients, D , with the concentration of protons, c , as measured from carefully calibrated spin counting experiments in the Nernst Einstein equation (Equation 1)

$$\sigma = \frac{cDz^2F^2}{RT} \quad [1]$$

We see that the predicted proton conductivities are close to the measured values. Only the UV-cured film would have practical proton conductivity under the conditions of no inlet humidification at 120°C.

FIGURE 2. Variation of proton conductivity for a series of P(SiW₁₁XV-co-butyl acrylate-co-1,6-hexanedioldiacrylate) films where X is <75 wt%.

FIGURE 3. Variation in morphology caused by thermal curing (left) and UV-curing (right) for a poly(SiW₁₁, 80V-co-butyl acrylate-co-1,6-hexanedioldiacrylate) film as shown by ESEM (top) and AFM (bottom).

TABLE 2. Self diffusion data from PFGSE NMR at 120°C and 56% RH, and proton conductivities calculated from the Nernst–Einstein equation ($\lambda = 1$) at both limiting (∞) and perfect (0) diffusion lengths of a 80 wt% HPA polymer.

Polymerization Method	$D(0) \times 10^5$ (cm ² s ⁻¹)	$D(\infty) \times 10^5$ (cm ² s ⁻¹)	$\sigma(0)$ (mS cm ⁻¹)	$\sigma(\infty)$ (mS cm ⁻¹)
Thermal	0.84	0.13	65	10
UV	2.48	0.95	191	73

Conclusions and Future Directions

- High proton conductivities of >0.1 S cm⁻¹ at 120°C and $<50\%$ RH can be achieved by fabricating films with >85 wt% HPA.
- The correct morphology is key to achieving high proton conductivities and can be controlled by process conditions.
- Future work will focus in transferring this technology to new more practical polymer systems that will be optimized not only for proton conductivity, but also oxidative stability and mechanical strength.

FY 2009 Publications/Presentations

1. “Pushing polypolyoxometalates to their limits of proton conductivity.” J.L. Horan, S.F. Dec, M.C. Kuo and A.M. Herring, *Prepr. Pap.-Am. Chem. Soc., Div. Fuel Chem.*, **2008**, 53, 756.

2. “Using Heteropoly Acids to Enable PEM Fuel Cell Technology.” A.M. Herring, invited oral presentation, presented at Illinois Institute of Technology, Chicago, IL, October 2008.

3. “Pushing polypolyoxometalates to the limits of their proton conductivity.” J.L. Horan, A.M. Herring, S.F. Dec, M.C. Kuo, oral presentation, presented at the 214th ECS Meeting, Honolulu, HI, October 2008.

4. “Pushing Proton Conductivity to the Limit in a Series of POM Polymers.” A.M. Herring, J.L. Horan, M.-C. Kuo, S.F. Dec, M.H. Frey, A. Genupur, L. Ren, M.A. Yandrasits, and S.J. Hamrock, “Proton Exchange Membrane Fuel Cells VIII.” T. Fuller, K. Shinohara, V. Ramani, P. Shirvanian, H. Uchida, S. Cleghorn, M. Inaba, S. Mitsuhashi, P. Strasser, H. Nakagawa, H.A. Gasteiger, T. Zawodzinski, C. Lamy, Ed.s, *Electrochemical Society Transactions*, **2008**, 16, 699.

5. “A New Ionomer Based on Novel PolyPOM Materials.” A.M. Herring, J.L. Horan, M.-C. Kuo, S.F. Dec, M.H. Frey, A. Genupur, L. Ren, M.A. Yandrasits, and S.J. Hamrock., *Fuel Cell Seminar Abstracts*, **2008**.

6. “A New Ionomer Based on Novel PolyPOM Materials.” A.M. Herring, J.L. Horan, M.-C. Kuo, S.F. Dec, M.H. Frey, A. Genupur, L. Ren, M.A. Yandrasits, and S.J. Hamrock, Oral presentation, presented at the Fuel Cell Seminar, Phoenix, AZ, October 2008.

7. “An Ionomer With Very High Proton Conductivity Derived From The Co-Polymerization of H₂[SiW₁₁O₄₀(Si(CH=CH₂))₂] with Butyl Acrylate and Hexanediol Diacrylate.” J.L. Horan, A. Genupur, L. Ren,

B.J. Sikora, M.-C. Kuo, F. Meng, S.F. Dec, M.H. Frey, G.M. Haugen, M.A. Yandrasits, S.J. Hamrock, and A.M. Herring*, *Chem. Sus. Chem.*, **2009**, 2, 226.

8. "New composite proton exchange membranes for fuel cell applications based on polyPolyoxometalates." A.M. Herring, J.L. Horan, M.-C. Kuo, S.F. Dec, M.H. Frey, A. Genupur, L. Ren, M.A. Yandrasits, and S.J. Hamrock, invited keynote oral presentation, presented at the 2008 Fall MRS meeting, Boston, MA, December 2008.

9. "PolyPOM membranes for hot and dry PEM fuel cell operation." A.M. Herring and M.H. Frey, oral presentation, presented to the DOE Tech team, Detroit, MI, February 2009.

10. "Designing an Ionomer From Scratch – Pushing PolyPOMs to the Limit." A.M. Herring, invited oral presentation, presented at Advances in Polymer Electrolyte Membrane Fuel Cell Systems 2009, Asilomar, CA, February 2009.

11. "Novel Approaches to Immobilized Heteropoly Acid (HPA) Systems for High Temperature, Low Relative Humidity Polymer-Type Membranes." A.M. Herring, M.H. Frey, S.F. Dec, S.J. Hamrock, G. Haugen, M.A. Yandrasits, H. Ren, A. Genupur, M. Emery, M.-C. Kuo, J.L. Horan, S. Sachdeva, A. Perdue, B. Sikora, oral presentation, presented at the 237th ACS Meeting, Salt Lake City, UT, March 2009.

12. "Further Understanding of Polyoxometallate Modified Titania Electrodes for Photoelectrochemical Water Splitting." A.M. Herring, P. Vallett, M.-C. Kuo, T. Furtak, J.A. Turner and M.T. Lusk, presented at the 215th ECS Meeting, San Francisco, CA, May 2009.

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2. Malers, J.L.; Sweikart, M.-A.; Horan, J.L.; Turner, J.A.; Herring, A.M., *Journal of Power Sources* **2007**, 172, 83.
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V.D.12 Improved, Low-Cost, Durable Fuel Cell Membranes

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Subcontractors:

- Johnson-Matthey Fuel Cells, Inc., West Chester, PA
- University of Hawaii, Honolulu, HI
- Virginia Polytechnic Institute and State University (Virginia Tech), Blacksburg, VA
- Oak Ridge National Laboratory, Oak Ridge, TN

Start Date: September 30, 2007
Project End Date: September 30, 2010

Technical Targets

This project aims at developing low-cost, durable membranes, and membrane electrode assemblies (MEAs) according to the 2010 DOE goals:

- Cost: \$20/m²
- Durability: 5,000 hrs with cycling.

Accomplishments

Membranes

- New M43 membrane developed with improved conductivity (vs. M41) at all RHs.
- Novel membrane (M70) developed based on di-sulfonated monomer-based polyelectrolyte.
- Block polysulfone ether polymers (BPSH)-based polyelectrolytes blended successfully with polyvinylidene fluoride (PVDF).
- The PVDF in the BPSH-based membranes significantly reduced the amount of swelling.

MEAs

- M43 passed > 20,000-cycle target in RH cycling test.
- M70 MEA outperformed M41- and M43-based MEAs.
- M70 MEA performance equivalent to NR-211 at high and moderate RH conditions.

Objectives

- Develop a low-cost membrane capable of operating at 80°C at low relative humidity (RH) (<50%).
- Develop a low-cost membrane capable of operating at temperatures up to 120°C and ultra-low RH of inlet gases (≤ 1.5 kPa).
- Elucidate ionomer and membrane failure and degradation mechanisms via ex situ and in situ accelerated testing.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) Cost
- (B) Durability

Introduction

Proton exchange membrane fuel cells rely on perfluorosulfonic acid (PFSA) for the construction of the membranes. The cost of these materials is high, largely due to the complexity and the number of steps involved in their synthesis. In addition, they suffer other shortcomings such as mediocre mechanical properties, poor gas barrier properties, and insufficient durability for some applications.

Approach

Arkema's approach consists of preparing blends of PVDF and a sulfonated polyelectrolyte. In these blends, the two polymers are intimately mixed. The originality of Arkema's approach is to decouple ion conductivity from the other requirements. Kynar® (Arkema's trade name for PVDF) provides an exceptional combination of properties that make it ideally suited for a membrane

matrix. It exhibits outstanding chemical resistance in highly oxidative environments (such as hydrogen peroxide and bromine), as well as in extreme acidic environments (such as HF, HCl and H_2SO_4). Due to the exceptional electrochemical stability and mechanical toughness of Kynar® PVDF, it is widely used as matrix material in lithium ion batteries. Also, these novel materials potentially offer a much lower cost than PFSA (at equal production volume) because their preparation process is simpler.

In our previous report, we have described Arkema's M41 membrane and its properties including its excellent mechanical properties, low permeation to hydrogen, good proton conductivity, and good in situ performance (beginning of life, stability, etc.) at 80°C and 100% RH. The membrane was able to undergo short-term excursions at 120°C and open-circuit voltage hold testing at 90°C and 30% RH had shown improvement (3-4 times) over state-of-the-art PFSA membranes. However, limitations at low RH were shown and a new membrane, M43, has been developed with improved conductivity across the whole relative humidity range (Figure 1).

The process for fabricating this new membrane was validated, and hundreds of feet of high quality (defect-free) membranes were produced on a pilot line. The key relevant physical properties of the M43 membrane are equivalent to those of M41. The performance of the MEAs prepared from M43 is slightly lower than that of NR-211 at 80°C and high RH conditions (Figure 2). The M43 MEA resistance is higher than that of NR-211, as was expected from membrane conductivity data (Figure 1). Although the low RH performance of M43 MEA is improved over M41, it is still insufficient below 70% RH. However, M43-based MEA passed the criteria for RH cycling test (20,000+ cycles, Figure 3).

Considering the limitations described above, we have developed a new family of lower equivalent weight membrane (M70) that contains polyelectrolyte with

two sulfonic acid groups per monomer unit in order to improve both proton conductivity and water retention. The polyelectrolyte is hydrolytically stable at 80°C and we are optimizing the blending process with Kynar® PVDF and the membrane activation. The process conditions have a significant influence over appearance, morphology, and conductivity.

While the performance of the M70 is below that of PFSA-based membrane at low RH in terms of proton conductivity (Figure 1), we have initiated testing of laboratory-produced M70 membranes in MEAs, as we believe that ex situ proton conductivity is not the only factor contributing to MEA performance. M70-based MEA shows a polarization curve comparable to that

FIGURE 2. Polarization curve of M70, M43, and Nafion® NR-211 at 80°C and high (100%/70%) RH.

FIGURE 1. Ex situ proton conductivity of M41, 43, 70, and Nafion® NR-211 membranes as a function of RH at 80°C.

FIGURE 3. RH cycling test for M43 and Nafion® NR-211-based MEA at 80°C.

FIGURE 4. Polarization curve of M70, M43, and Nafion® NR-211 at 80°C and moderate (50/50%) RH.

of PFSA-based MEA (NR-211) at high (100/70%) and moderate (50/50%) RH, as illustrated in Figures 2 and 4.

In another area of research, we have successfully prepared membranes by incorporating BPSH60 polyelectrolytes, prepared by our partner at Virginia Tech, in our Kynar® matrix. The swelling in water is significantly reduced in these membranes, but still high enough to compromise the membrane conductivity. We also observed substantial polyelectrolyte leaching and morphology rearrangement. Copolymers with high ion exchange capacity have been shown to have good proton conductivity at low RH but poor mechanical stability and high swelling/leaching. The introduction of the crosslinkable groups into the polymer should address these problems.

Conclusions and Future Directions

Improved ex situ proton conductivity of new M43 membranes at high RH has led to improved MEA performance over our previous generation (M41). However, the performance below 70% is still insufficient, even though the M43-based membrane passes 20,000+ cycles in RH cycling test.

A new membrane generation, M70, was developed with improved ex situ proton conductivity across the RH spectrum. Laboratory prepared MEAs from M70 membranes showed equivalent performance to PFSA-based MEAs at high (100/70%) and moderate (50/50%)

RH. In parallel, we have successfully incorporated BPSH-based polyelectrolytes in our Kynar® matrix and have shown significant reduction in swelling. However, the effect still needs to be minimized in order for these membranes to have acceptable proton conductivity at low RH.

Based on these results, we will continue to optimize the M70 membrane and activation processes in order to maximize conductivity and MEA performance (especially at low RH). We will also optimize the synthesis of our M70 polyelectrolyte monomer for the purpose of scaling up and preparing pilot line-based membranes for further testing and sampling to Johnson-Matthey. With continued promising results, larger MEAs will be supplied to the University of Hawaii for further testing.

To limit swelling and potential leaching of the BPSH polyelectrolyte, Virginia Tech is developing BPSH-based materials with higher ion exchange capacities containing amine or tetraepoxide functional groups that are suitable for crosslinking. We will incorporate these new materials in our process and evaluate the resulting membrane properties in MEAs as they become available.

We will also study M70 and BPSH-based membrane morphology at Oak Ridge National Laboratory and determine structure/property relationships. New families of polyelectrolytes will be prepared and tested if the performance of M70 and BPSH-based MEAs are deemed insufficient.

FY 2009 Publications/Presentations

1. "Improved, Low-Cost, Durable Kynar® Fuel Cell Membranes" presentation to the DOE Team – Golden, CO 1/27/2009. M. Foure, J. Goldbach, W. He.
2. "PVDF/Phosphonated Polyelectrolyte Blend Membranes". Advances in Polymer Electrolyte Membrane Fuel Cell Systems 2009 – Pacific Grove, CA 2/16/2009.
3. "Improved, Durable, Low-Cost Fuel Cell Membranes" presentation to Freedom CAR Tech Team – Detroit, MI 10/07/2008 – J. Goldbach, W. He.
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5. "State-of-the-Art and Challenges in Polymer Electrolyte Fuel Cell Membranes. NIST NSMC joint meeting – Gaithersburg, MD 11/06/2008 – J. Goldbach.

V.D.13 Membranes and MEAs for Dry, Hot Operating Conditions

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Project End Date: March 31, 2011

Technical Targets

Table 1. Progress towards Meeting Membrane Technical Targets

		3M	2010 Target	2015 Target
		2009 Status		
Conductivity at 120°C	S/cm	0.146 (46% RH)	0.1	0.1
		580 EW PFSA		
Conductivity at 80°C	S/cm	0.1 (39% RH)	0.1	0.1
		0.13 (50% RH)		
		0.50 (92% RH)		
Conductivity at 30°C	S/cm	0.1 (80% RH)	0.07	0.07
		580 EW PFSA		
Conductivity at -20°C	S/cm	0.014 S/cm	0.01	0.01
		700 EW PFSA		
O ₂ cross-over	mA/cm ²	<0.5	2	2
		20 μM Membrane		
H ₂ cross-over	mA/cm ²	<2	2	2
		20 μM Membrane		
Durability w/ cycling	Hours	12,000 (80°C)	5,000 (80°C)	5,000 (80°C)
		1,000 (120°C)		
OCV Lifetime	Hours	500	200	200
		825 EW PFSA		
Humidity cycles	Cycles	> 20,000 Un-reinforced Membrane	20,000	20,000

RH – relative humidity; EW PFSA – equivalent weight perfluoro sulfonic acid; OCV – open-circuit voltage

Objectives

To develop a new proton exchange membrane with higher proton conductivity and improved durability under hotter and drier conditions, in order to meet DOE Hydrogen, Fuel Cells and Infrastructure Technologies Multi-Year Research, Development and Demonstration Plan 2010 commercialization targets for automotive fuel cells.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section (3.4.3) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) Durability
- (C) Performance

Accomplishments

- Conductivity, fuel cell and diffusion measurements on a broad range of EWs and varied side-chains have provided insight into structure/conductivity relationships.
- We have synthesized new two and three acid-per-sidechain ionomers. These show:
 - Enhanced conductivity vs. starting PFSA.
 - High hydrolytic stability (no hydrolysis > 1 week in hot H₂SO₄ or in 250°C H₂O).
- Hetero poly acids (HPAs) have provided enhanced conductivity and chemical resistance. Model compounds show we can form a stable linkage

which may allow water stable HPA containing ionomer membranes.

- 825 EW 3M ionomer with new additives and optimized fabrication process provides:
 - >20,000 cycles in %RH cycle test.
 - >500 hours in OCV test.
 - >12,000-hour membrane electrode assembly (MEA) lifetimes in accelerated tests.
- Dissipative particle dynamics (DPD) simulations show morphologies consistent with clipped random wave (CRW) analysis of small angle X-ray scattering (SAXS) data and conductivity measurements.
- Polymer and model compound stability studies are providing insight into degradation pathways and relative stability.

Introduction

Proton exchange membrane fuel cells (PEMFCs) represent a promising power source for a variety of applications. While many breakthroughs have been made over the last few years in the development of PEMFCs, technical and economic barriers for their commercialization still exist. Key areas where improvements are still needed are in expanding the temperature range and lowering the humidification requirements of the stack [1]. Requirements of system size, efficiency, performance, start-up and cooling mean that fuel cells must be able to run robustly and exhibit adequate durability under a wide variety of operating temperatures, including temperatures up to 120°C. They must also be able to do this with little or no external gas humidification (i.e., “dry”), and during start-up, shut-down, or periods of lower stack temperatures, they must run in the presence of, and be stable to, some liquid water in the gas channels. Unfortunately, operation under these hot, dry conditions seriously compromises both the conductivity and durability of the ionomer membrane.

The objectives of this collaborative effort are to develop new proton exchange membranes (PEMs) for fuel cells capable of providing excellent durability and performance while operating under low humidification conditions and at temperatures ranging from -20°C to 120°C. Success on this project should result in PEMs with the performance and durability characteristics required for the development of fuel cells which meet commercialization targets for the automotive industry and other fuel cell applications. The processes for making the new membranes, and the MEAs comprising them, should be scalable for manufacturing at high volumes and at costs that can meet industry targets.

Approach

The focus of this project is to develop a new PEM which can operate under hotter, drier conditions than the state-of-the-art membranes today. These membranes and MEAs made from them should meet the 2010 DOE technical targets for performance and durability. Activities include:

- Synthesize and test new polymer membranes, including both fluorinated and non-fluorinated polymers as well as composite or hybrid systems, and evaluate their conductivity and chemical and mechanical stability.
- Evaluate new membrane manufacturing methods for increasing membrane mechanical properties and improving MEA lifetime.
- Develop new membrane additives aimed at increasing conductivity and improving membrane stability/durability under these dry conditions.
- Perform both experimental and theoretical studies of factors controlling proton transport and mechanisms of polymer degradation and factors affecting membrane durability in an MEA.
- Focus on materials which can be made using processes which will be scalable to commercial volumes using cost effective methods.

Results

Membranes based on the 3M Ionomer (Figure 1a) have been prepared with a variety of EWs (grams polymer/moles acid). Figure 2 shows the conductivity of some of these PFSA as a function of EW at 80°C, and at a number of different hydration, or λ values (λ represents the number of water molecules absorbed per sulfonic acid group, determined gravimetrically). It can be seen that at lower humidification levels, the impact of EW on conductivity is greater than at higher humidification. This suggests that the hydrated acid groups may be more accessible to one another in the lower EW ionomer, allowing proton transport even with little or no “free” water. Another observation consistent with this is that pulsed-field gradient spin-echo nuclear magnetic resonance (NMR) measurements of proton diffusion coefficients show that for the lowest EW ionomers, the diffusivity decreases by a smaller amount as the water content decreases, compared to higher EW membranes. It is worth noting that the low EW ionomers have higher conductivity than the model compound perfluorobutane sulfonic acid, indicating the importance of the phase separated structure of the PFSA.

New membrane fabrication processes have allowed the fabrication of ionomer membranes with EWs of about 800 which can meet the %RH cycle target of 20,000 cycles without any mechanical stabilization or reinforcement.

FIGURE 1. Structure of selected ionomers based on the 3M Ionomer. 1a: PFSA, 1b: Trifluoromethyl Imide, 1c: Phenyl Imide, 1d: Ortho Bis Acid, 1e: 1D Meta Bis Acid.

While lower EW ionomers provide higher proton conductivity under drier conditions, the mechanical integrity of these membranes is poor. The 3M ionomer swells excessively at EWs below about 750 and becomes water soluble at EWs below about 650. This is near the EW at which the tetrafluoroethylene (TFE) segments in the polymer backbone are too short to crystallize, as measured by wide angle X-ray scattering. One way to produce polymers with long enough TFE segments in the backbone for crystallization and low enough EW to provide high conductivity is to have more than one protogenic hydrogen on each functional sidechain.

FIGURE 2. Conductivity of 3M PFSA ionomers as a function of EW for assorted humidification (λ) values.

FIGURE 3. Conductivity of selected ionomer membranes as a function of %RH at 80°C.

Towards that end, we have prepared several bis sulfonyl imide polymers, some of which are shown in Figures 1b-e.

PFSA's with the sulfonic acid group replaced with a bis sulfonyl imide group have been described before [2]. They benefit from increased conductivity due to increased acidity. Figure 3 shows that a bis-trifluoromethyl imide with an EW of about 800 (1b) has conductivity much higher than an 800 EW PFSA, and has conductivity close to that of a 650 EW PFSA. However, the sidechain of this imide has a higher MW than the sulfonic acid sidechain in a PFSA. To prepare this ionomer, a polymer precursor (that is the sulfonyl fluoride form of the polymer) with an EW of 650 was used. The ultimate result is a trade-off, where the increase in EW due to the increase in sidechain MW is offset by the higher conductivity from the increase in acidity, and there is no net gain in conductivity. In other words, a 650 EW polymer precursor has been converted to an 800 EW ionomer with the conductivity of a 650 EW PFSA. The

use of an imide having multiple protogenic hydrogen overcomes this dilemma. Our approach is to prepare ionomers based on the phenyl imide (1c). This parent compound suffers from the same drawback as the perfluorinated analog, 1b, in that we are increasing the MW of the sidechain. Further, this imide does not have the enhancement in conductivity due to increased acidity, as this mixed fluorocarbon/hydrocarbon imide acid has a pKa similar to a PFSA. Figure 3 shows that the 800 EW phenyl imide has conductivity which is similar to the 800 EW PFSA at high %RH, but the conductivity drops off precipitously at lower %RH, and the conductivity of this material is more than 1,000 times lower than the PFSA at 35% RH. This is due to a large degree from significant drying out of this ionomer at low humidity, and at 35% RH the value of lambda for this material is about 0.5, compared to 2 for the 800 EW PFSA. Attachment of additional sulfonic acid groups to the benzene ring improves the conductivity of this type of imide dramatically. Figure 3 shows conductivity for compounds 1d, 1e. These bis acid compounds were prepared from an 800 EW starting polymer, but have an EW of about 550, as the EW of the polymer is “cut in half” when the sidechain is modified to have two protogenic groups. These polymers do have higher conductivity than their precursor at RH above about 40%. They do show a small downward curvature in the low RH region, possible due to morphological differences between this polymer and the PFSA. Since these polymers were prepared with an 800 EW precursor polymer, the backbone crystallinity provides lower swelling and better mechanical properties at higher humidification. We have recently prepared a 450 EW ionomer with an average of about 2.5 protogenic hydrogens per sidechain which has shown an additional increase in conductivity.

DPD simulations [3] have been used to investigate the effects that these different protogenic groups may have on the hydrated morphology of membranes with the same backbone chemistry. This is done to gain a better understanding of the relationship between proton transport and the polymer structure. Initial investigations of the hydrated morphologies of the three different ionomers shown in Figures 1a, 1c and 1d show that there are significant differences between these materials in the size and shape of the water clusters at several different hydration levels. In the case of the PFSA polymers, the morphologies from these simulations are in good agreement with morphologies derived from CRW analysis of SAXS experiments done on the ionomer at different hydration levels [4]. Similar experiments on the other ionomer structures are currently being carried out.

We have investigated the degradation pathways for these PFSA and ionomers by studying the ex situ degradation of ionomers and model compounds using electron spin resonance (ESR) spectroscopy and high pressure liquid chromatography/mass spectroscopy. A

kinetic approach, using ESR spectroscopy, has been used to compare the stability of Nafion® and 3M Ionomer as aqueous dispersions to attack by hydroxyl radicals generated by ultraviolet (UV)-irradiation of H₂O₂ solutions [5]. Hydroxyl radicals and carbon-centered radicals derived from the membranes were detected as adducts of 5,5-dimethylpyrroline-N-oxide (DMPO) as the spin trap [6,7]. Once generated by UV-irradiation of H₂O₂, HO• radicals can be trapped by the spin trap (reaction 1 below), or react with membranes or other competitors (C in reaction 2 below). The concentration of HO• radicals depends on the reaction rates of these parallel reactions, and can be measured by tracking the intensity of the ESR spectrum of the DMPO/OH adduct as a function of time during UV-irradiation of a solution containing the spin trap and the competitor.

The reaction rate constant for the reaction of HO• radicals with the competitor can be deduced from equation 3 below [8,9]

$$V/v - 1 = k_c[C]/k_{\text{DMPO}}[\text{DMPO}] \quad (3)$$

where V and v are initial reaction rates of DMPO/OH adduct formation in the absence and presence of competitor (membrane), and $[C]$ and $[\text{DMPO}]$ are the competitor and DMPO concentrations, respectively. Therefore, by plotting $V/v - 1$ vs. $[C]/[\text{DMPO}]$ we can determine k_c/k_{DMPO} . The results, shown in Figure 4, have indicated that the rate constant for the reaction of

FIGURE 4. Membranes as competitors for HO• radicals. Membrane concentrations were expressed as the concentrations of sulfonic groups. The 3M Ionomer and the ionomer labeled “Stabilized Nafion®” have been stabilized via carboxylate end-group removal.

hydroxyl radicals with the 3M membranes is significantly slower compared to that for Nafion®.

New inorganic membrane/MEA components have also shown promise in stabilizing membranes both in ex situ tests and in fuel cell tests. MEAs prepared with these new membranes have archived lifetimes in accelerated tests in excess of 12,000 hours.

Conclusions and Future Directions

Our focus in the first portion of this project has been on new polymers and new stabilizing or conductivity enhancing membrane components. We have also focused on gaining a better understanding of structure property relationships relevant to conductivity and durability. We have met all of the DOE membrane targets with at least one of the materials tested, and we have a clear path toward materials which can meet all of the targets. While low EW ionomers have inadequate stability with liquid water, multi acid sidechains show promise as a pathway towards membranes which can meet both conductivity and durability targets. Future activities include:

- Continue preparation and evaluation of the conductivity and durability of low EW PFSA, new imide containing polymers and membrane additives.
- Continue to probe factors in transport using NMR relaxation and diffusion, SAXS, conductivity, modeling and other spectroscopic measurements. Continue to develop a better understanding of effect of low lambda on proton transport.
- Evaluate impact of new protogenic groups, multi-acid side-chains and additives on membrane oxidative and chemical stability using ESR, ex situ tests, model compound tests and fuel cell tests. Investigate the structural basis for the higher stability of 3M membranes compared to Nafion® in ESR experiments.
- Evaluate membranes crosslinked in both the hydrophilic and hydrophobic regions.
- Provide water stable membranes comprising HPAs.
- Develop a better understanding of role of crystallinity on swelling in new polymers using X-ray scattering, mechanical properties testing and modeling.
- Evaluate additional stabilizers (including new HPA based stabilizers).
- Describe degradation pathways and rates for current group of model compounds and correlate with membrane stability.

FY 2009 Publications/Presentations

1. Niccolo V. Aieta, Ronald J. Stanis, James L. Horan, Michael A. Yandrasits, David J. Cookson, Bridget Ingham,

Steven J. Hamrock, and Andrew M. Herring “*Clipped Random Wave Morphologies and the Analysis of the SAXS of an Ionomer Formed by Co-Polymerization of Tetrafluoroethylene and CF₂=CFO(CF₂)₄SO₃H.*” *Macromol.*, in press.

2. Michael A. Yandrasits and Steven J. Hamrock “*Membranes for PEM Fuel Cells*” in “ACS Symposium Series: Fuel Cell Chemistry and Operation I”, in press.

3. Gregory Haugen, Michael Emery, Steven Hamrock, Michael Yandrasits, and Sara Barta “*Open Circuit Voltage Fuel Cell Durability Testing using Multiple PEM MEAs*” in “ACS Symposium Series: Fuel Cell Chemistry and Operation I”, in press.

4. Niccolo V. Aieta, Ronald J. Stanis, James L. Horan, Michael A. Yandrasits, David J. Cookson, Bridget Ingham, Steven J. Hamrock, and Andrew M. Herring “*Clipped Random Wave Morphologies Derived From SAXS Of Differing Equivalent Weights Of The 3M Ionomer : A New Way To Visualize Copolymers*” *Advances in Materials for Proton Exchange Membrane Fuel Cell Systems*; Pacific Grove: California, February 17, 2009.

5. Sonny Sachdeva, Neeraj Sharma, Steven J. Hamrock, and Andrew M. Herring, “*Characterization Of Heteropolyacid Immobilized Proton Exchange Membranes*” *Advances in Materials for Proton Exchange Membrane Fuel Cell Systems*; Pacific Grove: California, February 17, 2009.

6. Steven J. Hamrock, “*Proton Exchange Membrane Development at 3M*”, *Advances in Materials for Proton Exchange Membrane Fuel Cell Systems*; Pacific Grove: California, February 16, 2009.

7. David Schiraldi, “*Durability of Non-perfluorinated Membrane Materials for Fuel Cells*” *Advances in Materials for Proton Exchange Membrane Fuel Cell Systems*; Pacific Grove: California, February 16, 2009.

8. Shulamith Schlick “*Fragmentation of Proton Exchange Membranes Used in Fuel Cells: Direct ESR and Spin Trapping Methods*” *Commissariat à l’Energie Atomique (CEA)*, Grenoble, France, October 23, 2008.

9. Niccolo V. Aieta, Mike A. Yandrasits, Steven J. Hamrock, Ronald J. Stanis, James L. Horan, and Andrew M. Herring “*Representative Morphologies of Nafion™ and Other PFSA Membranes Using a Fourier Transform Approach to the Reduction of SAXS Data at Different Levels of Hydration*” 214th ECS National Meeting, Honolulu, HI, October 12, 2008.

10. David Schiraldi, “*Chemical Durability Studies Of PFSA And Nonfluorinated PEM Materials*”, 236th ACS National Meeting, August 20, 2008, Philadelphia, PA.

11. Stephen J. Paddison “*Mesoscopic Modeling Of The Morphology And State Of Water In Hydrated PFSA Fuel Cell Membranes*”, 236th ACS National Meeting, August 18, 2008, Philadelphia, PA.

12. Michael Yandrasits, “*PEMFC Membrane Development At 3M*”, 236th ACS National Meeting, August 18, 2008, Philadelphia, PA.

13. Steven Hamrock, “*Membranes for PEM Fuel Cells*”, Gordon Research Conference - Membranes: Materials & Processes, August 11, **2008**, Colby-Sawyer College, NH.

14. D. Wu, S. J. Paddison, and J. A. Elliott, “*A Comparative Study Of The Hydrated Morphologies Of Perfluorosulfonic Acid Fuel Cell Membranes*”, *Energy and Environmental Science*, **2008**, *1*, 284-293.

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V.D.14 New Polyelectrolyte Materials for High Temperature Fuel Cells

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Technical Targets

This project is aimed at the development of membranes that do not require the presence of added water to achieve adequate conductivity (0.1 S/cm at 120°C, 0.07 S/cm at 20°C and 0.01 S/cm at -20°C). Studies are conducted on proton solvent molecules and protogenic acid groups that can be tethered to polymer matrices to provide solid state membranes through which only the proton moves. Such membranes with no mobile solvents are expected to have lower gas permeabilities that lead to lower cross-over currents (target is <2 mA/cm²). Since swelling with solvent (e.g. water) is also much reduced, durability goals should be more easily attained (target is 5,000 hours) due to reduced mechanical stress. However, durability of the solvent molecules and their tethers to the polymer matrix is an issue of great concern. Finally, the materials must also be suitable for the preparation of electrode structures so that suitable MEAs may be prepared and tested. Not only do the materials have to be compatible with conventional catalysts but the electrode structure has to function adequately (target 1,000 mW/cm²) in a medium of low water content where catalyst activity may be quite different from a high water content condition (target 720 μ A/cm² at 900 mV(Pt) or 300 A/cm³ at 800 mv (non-precious group metal catalyst). The provision of membranes and MEAs that need no humidification provides significant system simplifications and large cost advantages over conventional materials

Accomplishments

- Demonstrated that phase-separated polymer structures are essential in order to achieve practical conductivities (0.1 S/cm) with tethered heterocyclic bases such as imidazole to solvate the protons in place of water. These structures are best controlled through the use of block copolymers to control the backbone morphology.
- Demonstrated that short side chain tethers for the heterocyclic bases are necessary to facilitate fast proton transport by the Grotthuss mechanism.
- System modeling of the relative effects of Grotthuss versus segmental motion transport of the protons through the membrane shows that the overall conductivity is rapidly diminished by relatively small amounts of segmental motion bottlenecks.
- Degradation studies of imidazole-containing materials using metal ion initiated Fenton chemistry shows that the degradation is accelerated by the presence of the heterocyclic bases which act as ligands to the metal ions that decompose the peroxide to hydroxyl. It is concluded that

Objectives

Develop durable water-free membrane materials with properties that meet the 2015 DOE targets:

- Conductivity: 0.1 S/cm at operating temperatures ($\leq 120^\circ\text{C}$) and inlet water vapor partial pressures <1.5 kPa.
- Durability with cycling $>5,000$ hours at $>80^\circ\text{C}$.
- Oxygen and hydrogen cross-over currents ≤ 2 mA/cm².
- Durable membrane electrode assemblies (MEAs) with rated power at 1,000 mW/cm² and less than 5% performance degradation over lifetime.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section (3.4.4) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (E) System Thermal and Water Management
- (C) Performance
- (A) Durability
- (B) Cost

ultraviolet/visible light or thermal initiation of peroxide decomposition will provide a more appropriate test.

- Studies of the behavior of imidazolium bis(trifluoromethylsulfonyl)imide (TFSI) ionic liquids in block copolymer matrices have demonstrated the effect of the proton-conducting medium on polymer morphology. The presence of the polymers structures appears to impose order on the conducting medium that promotes Grotthuss transport over longer distances and at lower temperatures by concentrating the ions in the channel structures. This results in conductivities >0.02 S/cm at 120°C and >0.01 S/cm at 85°C in the absence of any water.
- Composite electrodes and MEAs have been successfully prepared with non-Nafion[®] binder ionomers which perform almost as well as Nafion[®] MEAs in the absence of humidification. The best performing materials are fluorinated and the performance appears to be related to mass transport and flooding issues due to product water. This success is attributable to careful preparation of binder inks and appropriate formulations and demonstrates the capability to prepared MEAs with imidazole-containing materials in the coming year.

Introduction

Presently available fuel cell membranes require the presence of liquid water in order to transport protons and support the current demands. Because of the poor performance of fuel cell electrocatalysts, nearly half of the fuel energy is converted to heat which requires a very complex and expensive heat and water management system in order to maintain the water content of the membranes. Kreuer pioneered the investigation of alternative proton conducting solvents that could replace water and, in particular, reminded the research community of the ability of heterocyclic bases such as imidazole to support proton conduction [1]. It has also been recently discovered that nature uses imidazoles for the purpose of moving protons through membranes in living systems [2] and also uses imidazole groups to bind metal ions in oxygen reduction enzyme catalysts such as copper laccase [3]. It has also been noted previously that imidazole bases appear to be resistant to oxidation [4] by oxygen species, an important property for a fuel cell solvent. Previous work on the attachment of imidazoles to polyelectrolytes that showed that an all solid state proton conducting membrane was indeed possible [5]. While the conductivities achieved were low the polymer structures were not ideal and the purpose of this project is to understand how to optimize the polymer structures to achieve the desired properties.

Approach

Since the project involves the manipulation of a large number of molecular features of the target polymers, the approach taken is to use mixtures of easily obtained components to measure how the properties vary and to use these results to formulate the composition of the final polymer materials which are difficult to make. In the Fiscal Year 2008 annual report, measurements on proton conducting ionic liquids, both neat and dispersed in polymer matrices were described, as were measurements on polyelectrolyte materials doped with heterocyclic bases. Similar measurements have been continued on models that more closely resemble the tethered groups in the final target polymers and neutron scattering, and nuclear magnetic resonance (NMR) relaxation measurements have been added to study the mechanisms of proton transport. Models of the proton transport through the membrane have been constructed to isolate the consequences of bottlenecks due to slow proton transport and this knowledge helps guide the polymer synthesis and morphology control, which is critical to achievement of the conductivity goals, adequate mechanical properties and control of gas cross-over. Synthesis of polymer materials with imidazole attached to side chains has been carried out and these polymers have been blended with polymer bound acids to give fully tethered materials using the results with the model ionic liquids to formulate the relative concentrations of imidazole and acid. Conductivity, water uptake and degradation studies are carried out on both the models and the completed fully-tethered polymers. Since the synthesized membrane materials must be used with electrodes to be useful, methods of preparing composite electrodes with novel, non-Nafion[®] binders are investigated to determine the polymer properties that lead to good electrode performance. Less expensive ionomer materials are used first to develop the methodology to be applied with the target imidazole-containing ionomer materials..

Results

Figure 1 shows a schematic of the type of polymer structure that appears to be desired in order to achieve fast proton transport through the membrane. The results obtained in the past year on ionic liquid models and on synthesized polymers with tethered imidazoles indicate that the morphology shown is necessary to promote the Grotthuss mechanism of proton transport. For this it is necessary to develop phase separation so that a pore-like structure is formed to provide some order for the imidazole structures to rapidly transport protons via a hopping mechanism. The phase separation is best controlled by use of block copolymers and by use of appropriate backbones. Figure 1(b) shows examples of

FIGURE 1. (a) Schematic representation of desired polymer morphology to promote high conductivity based on results obtained in FY 2009. (b) Examples of polymer structures prepared and under study FY 2009.

some of the polymer structures that have been prepared for this purpose and which are under continuing study.

Particularly noteworthy is the imidazole group (e.g. Z in Figure 1) which is shown as tethered to the polymer through the 2-position. The tether can also be through the 4- or 5-positions. However, the tether cannot be through the 1-position, which is the nitrogen as this would block the operation of the Grotthuss mechanism of proton transport. The mechanism is shown schematically in Figure 1(a) where the arrows represent electronic rearrangements within the imidazole molecules and rotation around the tether bonds. The end result is that the proton is able to hop from one side to another without the need for the solvent molecules to move with it. The attachment of the imidazole through positions other than the nitrogen is not trivial and requires the use of protecting groups on the nitrogen which can be cleanly removed once the polymer is prepared. Considerable effort has been expended upon this problem during FY 2008 and FY 2009 and a completely satisfactory solution is still not in hand. In this, the project contains much in common with peptide chemistry and we are drawing heavily on knowledge from that field to assist in the problem.

Figure 2 shows the results of conductivity measurements made on polymers that contain the imidazole tethered in the 2-position. These measurements are made under completely dry conditions. The polymers are blended either with trifluoromethylsulfonic acid (TFA) or Nafion® where the numbers 1:1, 4:1 or 10:1 represent the ratio of the imidazole molecules to the acid groups. The blends with Nafion® ionomer represent fully immobilized materials where only the proton moves through the membrane. The figure shows results for a polymer backbone which can phase separate (polystyrene) (a) and one which does not (polyether) (b) and each graph shows comparisons of conductivities for short side chains versus long side chains. It can be seen that the short side chain with the polystyrene backbone provides the highest conductivity at 120°C (nearly 10^{-2} S/cm) but with a strong temperature dependence. A similar temperature dependence is observed with the non-phase-separating polymer (imiepi:Nafion®-4:1) but at a lower absolute value of conductivity. This may indicate that the bottleneck for proton transport lies in transport through portions of the polymer which is controlled by segmental motion and that the phase separation may concentrate the ionic conduction medium to achieve a higher local

VBCL-ABOH

Proton conductivity of imidazole tethered polymers with styrene backbone with and without silyl linker

ImiVBCL

(a)

Proton conductivities of polymers with long versus short side chains

imiepi

(b)

epiaboh

FIGURE 2. Conductivity measurements as a function of temperature of tethered imidazole polymers blended with TFA and Nafion®. (a) Polystyrene backbones thought to promote phase separation; (b) polyether backbones thought not to phase separate. Polymer structures shown.

concentration of charge carriers which can support higher conductivities. The hypotheses concerning the effect of phase separation and side chain length are under continuing study but it appears reasonable that conductivity's in the range of 0.01-0.1 S/cm at 120°C are attainable by appropriately altering the polymer structures.

The temperature dependences of the conductivities shown in Figure 2 are clearly unacceptable for use at lower temperatures. Figure 3(a) shows much more desirable conductivity behavior for imidazolium TFSI ionic liquids (b) both as neat liquids and dispersed in a block copolymer matrix. Small angle X-ray scattering (SAXS) and small angle neutron scattering measurements carried out at LBNL and Oak Ridge National Laboratory respectively show how the presence of the ionic liquid alters the morphology of the polymer structure (Figure 3(c)) and these structures appear to correlate with the conductivity behavior in Figure 3(a). The pure ionic liquid (2VP:IL=0) shows a flat conductivity dependence upon temperature indicating a Grotthuss or "hopping" mechanism of proton transport. Addition of 40% block copolymer to the mix does not reduce the conductivity (2VP:IL=0.6) while the effect of 60% by weight of the polymer is relatively small (2VP:IL=1.36) and only when the polymer is present in

large excess (2VP:IL=3.63) does the conductivity drop to levels that are characteristic of control by segmental motion. The behavior of this sample is similar to the samples in Figure 2(b) which are not phase separated and charge transport is controlled by segmental motion.

To understand the conductivity results and also the impact of morphology, acid and base site concentrations, etc. on conduction, a network model has been developed. The network model uses pore-level effects such as changes in dielectric to corroborate the experimental findings and tune the resistances between the network nodes. These values will also be further explored in the future using model copolymer systems and NMR results. When complete, the network model will be able to ascertain the importance of bottlenecks on performance and provide guidance to the membrane synthesis efforts. As a first result, relatively simple calculations have shown that in a membrane with only a few linkages where the vehicle mechanism dominates, the overall conduction suffers greatly due to the much slower diffusion. These results are shown in Figure 3(d) which demonstrates that even a very small amount of vehicle motion (segmental motion in polymers) has a very significant effect upon the overall conductivity and this is magnified by the greater differences between Grotthuss and vehicle conductivities. Thus the presence

Conductivity of Block Copolymer: S-2-PVP (8.7-12.0kg/mol) in 5:5 IL

FIGURE 3. (a) Conductivity as a function of temperature of imidazolium TFSI ionic liquids in a poly(styrene-*b*-2-vinylpyridine) matrix for varying compositions; (b) structure of the studies ionic liquids and polymers; (c) SAXS measurements on ionic liquid-polymer mixtures; (d) Model of the effect of non-Grotthuss charge transport segments on overall conductivity.

of charge transfer bottlenecks can have severe effects upon the conductivity.

Finally, the polymer materials must eventually be tested in MEAs and to prepare for this, work has been carried out on the preparation of composite electrodes using non-Nafion® binders. Figure 4 shows the fuel cell performance of MEAs using ionomers with different levels of fluorination under fully humidified and non humidified conditions. The MEA with a PFSA-bonded cathode performed best, while the MEA using a wholly hydrocarbon binder performed the worst. MEAs using partially fluorinated ionomers gave an intermediate performance, with the performance depending on the degree of fluorination. These observations indicate that fluorination of ionomers improves fuel cell performance probably due to improved gas permeability. This effect is more prominent under non-humidified conditions which may indicate that rejection of water may be occurring allowing easier transport of the gases. In order to accomplish these results considerable experimentation

was required to formulate the electrode inks and patents have been applied for that describe this. These methods will be applied to the imidazole containing polymers as they become available.

Conclusions and Future Directions

Conclusions

- Conductivity measurements indicate that practical conductivities (0.05 S/cm) will be possible only through operation of the proton-hopping (Grotthuss) mechanism of charge transfer. This appears to be promoted by phase separation and morphology control. The morphology is best controlled by use of block co-polymers.
- Relatively simple model calculations have shown that in a membrane with only a few linkages where the segmental motion (vehicle) mechanism dominates, the overall conduction suffers greatly

FIGURE 4. Performance of different polymer binders (a) in humidified (b) and non-humidified (c) MEAs.

due to the much slower diffusion. This emphasizes the importance of control of the polymer morphology to avoid such bottlenecks.

- The use of metal-ion initiated Fenton chemistry for degradation studies of imidazole-containing polymers results in much more degradation than in the absence of the imidazoles. This is understandable due to the chelation of the ions by imidazole that results in a more active metal ion initiator. Ultraviolet/visible light or thermal initiation of peroxide decomposition is a more appropriate test but this indicates a vulnerability of imidazole polymers to the presence of metal ion contaminants.
- The preparation of composite electrodes for use in MEAs with non-Nafion® polymer binders requires considerable experimentation with ink formulation (concentration, solvent polarity and volatility, particle size, etc.) as well as processing conditions.

The development of the methodology is important for preparing MEAs with the imidazole bases present.

Future Directions

- Synthesis and measurements of polymers as functioning membranes is the highest priority.
- Stability of imidazole, the ionic liquids and the complete polymer architectures under oxidative conditions is a critical issue. Durability and degradation testing of membranes under fuel cell conditions is a priority.
- Preparation of MEAs is a critical issue as conventional electrodes will not allow a proper test to be carried out. Studies on this topic are already under way at LANL.
- Gas permeability and crossover measurements will be initiated.

- Modeling of the system and cell issues (conductivity, low catalyst activity at low relative humidity) will continue to guide experimentation. Molecular dynamics modeling needs to be added.

FY 2009 Publications/Presentations

- “New Polyelectrolyte Materials for High Temperature Fuel Cells”, John Kerr, DOE Hydrogen, Fuel Cells, and Infrastructure Technologies Program Review Meeting, May 9, 2009, Arlington, VA, presentation FC 14.
- “Polyelectrolyte Materials for Batteries, Fuel Cells and other Energy Applications”, John Kerr, Pennsylvania State University, Materials Science Distinguished Lecturer, March 26, 2009.
- “Water-free Proton Conductors”, John Kerr, LANL-NEDO Workshop, San Diego, CA, September 10, 2008.
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V.D.15 Development of Novel PEM Membrane and Multi-Phase CFD Modeling of PEM Fuel Cell*

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Project End Date: June 30, 2009

*Congressionally directed project

- (C) Durability
- (E) Thermal and Water Management

Technical Targets

This project is conducting fundamental studies to develop a new class of PEM materials capable of conducting protons at low RH. The multiphase CFD model will help to understand the underlying physics related to water and thermal management in PEM fuel cells. If successful, insights gained from these studies will be applied toward the design and manufacturing of advanced membrane materials that meet the following DOE 2010 membrane materials targets:

- Cost: \$20/m²
- Conductivity at operating temperature ($\leq 120^{\circ}\text{C}$): 0.1 S/cm
- Humidity range: $\leq 50\%$
- Area specific resistance: 0.02 Ohm/cm²
- Durability with cycling: at operating temperature ($\leq 80^{\circ}\text{C}$) – 5,000 hours
- Multiphase CFD porous flow model for designing improved water and thermal management strategies

Objectives

- Develop novel proton conducting membrane capable of conducting protons at low relative humidity (RH), withstanding temperatures in excess of 110°C and providing electrical insulation.
- Quantify extent of membrane performance enhancement compared to peer materials available in the market place.
- Reduce materials cost and develop simple manufacturing processes.
- Improve durability, dimensional stability, and thermal stability.
- Develop a computational fluid dynamics (CFD) multiphase porous flow model to understand thermal and water-transport phenomena in a single proton exchange membrane (PEM) fuel cell.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) Performance
- (B) Cost

Accomplishments

- Identified inexpensive membrane materials and developed simple manufacturing process capable of producing proton conducting membrane materials at a cost 60% below the DOE targets for 2010.
- Increased Proton Conductivity: In-house laboratory test shows that average 10 times increase in proton conductivity compared to peer materials (Nafion[®] 212) at 80°C (results presented in the last year DOE report). Though the third party (BekkTech) test results presented below show a lower conductivity than the in-house lab test, an updated version of our membrane sample is presently under testing at BekkTech to validate our lab test results. The updated results from BekkTech will be included in the final DOE report to be submitted soon.
- Reduced Resistance: An in-house laboratory test shows 71% lower resistance per unit area than peer (Nafion[®] 212) materials at 80°C (results reported to DOE last year).
- Reduced Induction Time: Induction time (time required to start proton transfer) is 70% lower than Nafion[®] 212.

- Low Membrane Water Content: Membrane able to conduct protons at low water content i.e. at low RH compared to peer materials (Nafion® 212) at 80°C.
- Developed and simulated multiphase porous flow model for CFD analysis of a single PEM fuel cell.
- Improved Prediction: Using two-phase CFD model results we developed a three dimensional (3D) control strategy for improved prediction of fuel cell stack performance while meeting the power demand.

Introduction

Currently, a benchmark commercially produced and widely used PEM for fuel cell applications is Nafion® [1]. Nafion® has a number of limitations such as an operating temperature range of 50°C~90°C [2] undesirable gas permeability - on the order of 10^{-6} cm²/s [3], which results in decreased fuel cell performance, limited operational hydration range [2-3] and high cost, \$800 per m² [1-3]. Additionally, Nafion® (polymer membrane) is easily degraded under high power and during on/off cycling. As such, polymer membranes need considerable improvement. Another concern is to thoroughly understand the water production and proton conduction mechanisms to minimize cathode electrode flooding and to ensure proper membrane hydration. The essential requirements of PEMs for fuel cell applications include the following: (i) high proton conductivity, (ii) minimal thickness (to minimize resistance resulting in fuel cell's ohmic drop), (iii) high thermal stability, (iv) excellent mechanical properties (strength, flexibility, and processability), (v) excellent chemical stability, (vi) low water drag, (vii) rapid adjustment of fast kinetics for electrode reactions, (viii) low or minimal gas permeability, and finally (ix) low cost and high availability.

In this project, using patented [4] polymer surface modification technology, a novel approach to the design and fabrication of PEMs has been developed whereby a non-structural polymer fabricated for proton exchange capacity is bound to an inert polymer matrix. This fabrication technique separates the proton exchange and structural requirements of the PEM allowing greater flexibility in proton exchange membrane design. To benchmark the performance of the membranes, we developed a theoretical model [5] to quantify several physical quantities such as proton exchange capacity (conductivity), resistance, induction time, and membrane water content. The results suggest a new route to fabricate cost-effective PEMs for fuel cell applications wherein one may focus more on the proton exchange capacity of the membrane allowing the structural properties of the membrane to be considered separately. To understand water and thermal management phenomena in an operational PEM fuel cell, we

developed a multi-phase CFD model and simulated it using finite element methods for an operational single PEM fuel cell. Using two-phase CFD model results we developed a 3D control strategy for improved prediction of fuel cell stack performance while meeting the necessary power demand.

Approach

- Use an inert, robust, mechanically and dimensionally stable polymer mesh that may be chemically modified on the surface to render it adhesive or chemically reactive.
- Use patented technology to prepare a proton exchange polymer media that has been designed primarily to have high proton exchange capability.
- Cast the proton exchange polymer media onto the robust polymer support to prepare the hybrid proton exchange membrane.
- Alter the composition of the proton exchange polymer media to optimize proton transport.
- Compare the performance of new PEM materials with the peer materials such as Nafion® 212.
- Validate multiphase CFD model results with the results published in the literature for a single PEM fuel cell.
- Using two-phase CFD model results, develop a 3D control strategy for improved prediction of fuel cell stack performance in order to meet the power demand.

Results

During the past year, the main focus has been the validation of membrane performance both at the laboratory scale and using industry-standard testing protocols. We sent our membrane samples to the BekkTech testing service, an industry-standard membrane sample testing service provider and obtained preliminary results regarding the membrane conductivity, resistivity, thickness measurements and RH cycling at 30°C, 80°C and 120°C. We analyzed the BekkTech test results and made necessary modifications. The efforts were mainly directed towards preparation of membrane samples in order to accommodate performance enhancement required in the operational PEM fuel cell environment. The entire process is currently underway. The water and thermal management issues of an operational single PEM fuel cell were also taken into account by validating the multi-phase CFD model with the results published in the literature. Using the two-phase CFD results, we developed and tested a 3D control strategy on a 5 kW PEM fuel cell stack (reported in quarterly report in 2009).

Figure 1a represents the 4-electrode conductivity versus RH at 30°C, 80°C and 120°C. From Figure 1a, we can see that our PEM membranes are able to

FIGURE 1. (a) 4-electrode conductivity test of our developed styrene-acrylonitrile-vinylsulfate type membrane with different relative humidity at 30°C, 80°C and 120°C. (b) SEM image of a styrene-acrylic acid-vinylsulfonate membrane – produced at Kettering facility.

conduct protons at different RH levels but required further improvement in terms of proton conductivity at reduced humidity conditions. Figure 1b represents the scanning electron microscope (SEM) image of our PEM membrane which shows the presence of proton conductive media on the inert mesh we used for mechanical and chemical stability of the membrane.

The water and thermal management issues of an operational PEM fuel cell are critical to enhancing cell performance because electrode flooding and membrane dehydration results in degradation of cell performance. For better understanding, we compared results of our multiphase porous flow model with the results available in the literature. Figure 2 presents the distribution of O_2 concentration in the cathode channel obtained using our multiphase porous flow model simulation (Figure 2a) with those obtained (Figure 2b) by Wang and Wang [6]. The color bar represents the concentration from highest (red) to lowest (blue) and the black arrows denote cathode gas velocity. As seen

FIGURE 2. Concentration distribution of gas phase (O_2) in the cathode channel. (a) 3D simulation of cathode with present multiphase model, (b) two dimensional (2D) model simulation of Wang and Wang [6] – two adjacent channels including bending regions of the serpentine channel. Black arrow indicates cathode gas velocity inside the channel.

from Figure 2, the O_2 concentration at the cathode inlet is the highest since fresh humidified air is supplied at the cathode. The O_2 concentration decreases along the gas channel from inlet to outlet due to the electrochemical oxygen reduction reaction (ORR) which results in water formation at the cathode. The depletion of O_2 along the cathode electrode is due to the electrochemical reaction which resulted in water production at the cathode. From Figure 2, we see a substantial amount of oxygen depletion in the regions far away from the inlet gas channel which resulted in the high current density. Comparing Figures 2a and 2b we see that the O_2 depletion trends along the gas channel are similar or comparable in terms of color bars. Thus we obtained a qualitative agreement between our multiphase flow model and that of the results reported by Wang and Wang [6]. In Figure 2b, we see a higher amount of O_2 concentration (see the values at the color bar, Figure 2b) at the inlet because of the requirements of maintaining the balance of the anode/cathode gas ratio. In our simulation, we only simulated the PEM fuel cell cathode. Addition of the anode portion into our simulation will be considered in the next step.

Figure 3 presents the concentration distribution of liquid phase (H_2O) in the cathode channel obtained

FIGURE 3. Concentration distribution of liquid phase (water) in the cathode channel. (a) 3D simulation of cathode with present multiphase model, (b) 2D model simulation of Wang and Wang [6] – two adjacent channels including bending regions of the serpentine channel. Black arrow indicates cathode gas velocity inside the channel.

using our multiphase porous flow model simulation (Figure 3a) with those obtained (Figure 3b) by Wang and Wang [6]. The color bar represents the concentration from highest (red) to lowest (blue) and the black arrow denotes cathode gas velocity. From Figure 3, we see that the concentration of liquid phase (water) at the cathode inlet is the lowest since humidified air, which has small water vapor content only (no liquid water), is supplied at the cathode. The liquid phase concentration is increasing along the gas channel from the inlet to the outlet due to the ORR over the cathode electrode to produce liquid phase (water). The depletion of O_2 along the cathode electrode produced liquid water through the electrochemical reaction at the cathode. Hence the liquid phase concentration increased along the gas channel. From Figure 3, we see that the liquid phase concentration increases substantially in larger amount in the regions far away from the inlet gas channel. Comparing Figures 3a and 3b, we see that the trend of increasing liquid phase concentration along the gas channel is similar. This indicates a qualitative agreement between our multiphase flow model and that of the results reported by Wang and Wang [6], although in Figure 3b we see a higher concentration of liquid phase water (see the values at the color bar, Figure 3b) at the outlet because of the requirements of maintaining the

balance of the anode/cathode gas ratio. A higher supply of reactant gases which increases the reaction rate results in higher liquid phase concentration. The liquid phase concentration increases along the far end of the channel due to the production of liquid water through the electro-chemical reaction. In our simulation, we only simulated the PEM fuel cell cathode. Addition of the anode portion into our simulation will be considered in the next step. The parametric values used in the simulation for the results presented in Figures 2 and 3 are listed in tables in [6-7]. The predictions obtained from the two-phase flow model (Figures 2a and 3a) will be beneficial to improve PEM fuel cell designs.

Implementation of Control Algorithm: Using the multi-phase CFD model results given in Figures 2 and 3, a 3D surface map of RH, pressure at the cathode and current density at different voltages of the PEM fuel cell stack was developed and tested for a 5 kW stack. Figure 4a shows the surface map for a voltage of 0.7 V. At this voltage, the current density varies from 440-550 mA/cm² depending on cell conditions (RH, pressure, etc.). Using the current density, we can calculate the stack power from the following equation:

$$P_{stack} = I_{stack} * n * V_{op} * A \quad (1)$$

where P_{stack} = total stack power, I_{stack} = stack current, V_{op} = cell operating voltage, n = number of cells in the stack and A = cross sectional area of the fuel cell. This gives us the range of power at which we can operate the fuel cell stack at this voltage. For different voltages, we can calculate the power and we can obtain a lookup table for the power demand with operating voltage. On the green-light test stand at Kettering Center for Fuel Cell Systems and Powertrain Integrations, the fuel and oxidant gases were supplied at a higher pressure. The energy needed for compression has to be supplied by the fuel cell itself. To obtain the power demand for the compressor, CHEMCAD simulation software was used to calculate the power based on the anode and cathode flow rates and compression ratios. By subtracting the compressor power from the fuel cell stack power we can obtain the net power that can be provided by the fuel cell stack. Figure 4b shows both the stack power and net power for a cell voltage of 0.7 V. Based on the net power, we can develop a lookup table between the operating voltage and power demand. So, for a particular power demand we can calculate the optimum operating pressure and humidity. The feed forward control strategy developed here calculates this optimum operating point and sends it as an input to the fuel cell stack. The steps followed to obtain the optimum operating points are:

- Determine the power demand.
- Calculate the appropriate operating voltage (V_{op}) based on the range of power demand from the lookup table.

FIGURE 4. (a) Surface map of the variation of current density with pressure and relative humidity at a constant voltage of 0.7 Volts for 5 kW stack. (b) Surface map of stack power and the net power that can be provided by the stack at a voltage of 0.7 Volts for 5 kW stack.

- From the surface map for net power at the selected voltage, calculate the minimum pressure P_{op} and RH (RH_{op}) at which you can get the required power demand.
- From the surface map we can calculate the corresponding P_{stack} for the selected operating pressure and RH (P_{op} , RH_{op}).
- Calculate I_{stack} from P_{stack} using equation 1 and send I_{stack} , P_{op} , RH_{op} as input to the system.

For a gas of known or desired humidity, we can calculate the pressure to operate the fuel cell stack from the 3D surface map of current density, humidity, and pressure as shown in Figure 4a. Then the pressure can be used in a feed forward control algorithm to meet the power requirement. As such, we can operate the fuel cell stack with a humidity driven power management strategy. For a gas of known humidity, for example 90%, the control algorithm was modified to search along a particular RH.

Conclusions and Future Directions

The past year has resulted in a great knowledge expansion regarding manufacturing processes of new PEM materials, laboratory-based and industry-standard

testing of membrane properties and multiphase CFD analysis of operational PEM fuel cells. We now understand the manufacturing process of new materials and the performance validation protocols in quantitative terms at least at the laboratory-based manufacturing stage. We have a good understanding of the polymer chemistry, thermodynamics and electro-kinetics. This information is critical to develop new membrane materials for fuel cell applications where chemical treatment, polymer casting, and performance evaluations are of the utmost importance. We also gained insight into the water and thermal management issues in the PEM fuel cell through multiphase CFD analysis. This year we intend to submit a final project report after finishing the evaluation of membrane properties using industry-standard characterization protocols which will help us to finalize the membrane materials with detailed membrane manufacturing process. We also will finalize the water and thermal management phenomena study in a PEM fuel cell.

Although the DOE deliverables of our project to date have been achieved, the following membrane attributes are necessary to further evaluate the membrane performance:

- Refining the manufacturing process to reduce the cost and use of low cost raw materials.
- Characterizing of membrane properties such as conductivity, resistivity, and thermal stability over the entire temperature and humidity range (e.g., operation up to 120°C) using industry standard protocols.
- Implementing CFD multi-phase porous flow model in a single fuel cell as well as fuel cells stack for improvement of water and thermal management design strategies.

Special Recognitions/Patents Issued

- Susanta K. Das, Jayesh Kavathe, Panini Kolavennu and K. Joel Berry, Novel design of fuel cell bipolar plate for optimal uniform delivery of reactant gases and efficient water removal, U.S. Patent Application, 2009 (Under Process - pending).
- Susanta K. Das, Jayesh Kavathe and K. Joel berry, Novel stack design and assembly of high temperature PEM fuel cell, U.S. Patent Application, 2009 (Under Process - pending).

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- Susanta K. Das, Panini Kolavennu, J. Hedrick, Beholz, L., Ali R. Zand and K.J. Berry, Synthesis and Characterization of a Composite Membrane for Polymer Electrolyte Fuel Cell, *Journal of Fuel Cell Science and Technology*, vol. 6, p. 011021-1~011021-6 (2009).

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3. Susanta K. Das, Antonio R. and K.J. Berry, Experimental Evaluation of CO Poisoning on the Performance of a High Temperature PEM Fuel Cell Stack, *Journal of Power Sources*, 2009 (in press- online available).
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V.D.16 Alternate Fuel Cell Membranes for Energy Independence*

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*Congressionally directed project

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

(B) Cost

(C) Performance

Technical Targets

- Synthesize novel membrane polymers and fabricate membrane electrode assemblies (MEAs).
- Achieve DOE area specific resistance goals.
- Attain good MEA performance in fuel cells.
- Attain good MEA operation at higher temperature (>100°C).
- Investigate physical and chemical durability (ex situ and fuel cell - in situ accelerated and long term tests, including relative humidity [RH] and temperature cycling).
- Identify MEA degradation mechanisms.
- Low-cost membranes.

Objectives

- Combine desirable qualities of Nafion® and sulfonated poly(arylene ether sulfone) (sPAES) polymers in new comonomers for use in proton exchange membrane fuel cells (PEMFCs).
- Develop synthetic strategies for sPAES comonomers containing perfluoroalkyl sulfonic acid moieties using fairly inexpensive and readily available reagents.
- Reproduce existing sPAES polymer membrane forms and establish benchmark data regarding performance and durability against which the novel membranes will be prepared.
- Compare fuel cell performance of our new comonomer membranes with Nafion® benchmark performance data.
- Understand the coupling between hydration microstructure, proton migration and morphology at temperatures above 100°C for Nafion® benchmark membranes.
- Establish the same for novel synthesized membranes and correlate results with membrane performance at high temperatures.
- Perform accelerated fuel cell in situ studies of membrane degradation.
- Affect inorganic oxide in situ modification of Nafion® membranes to improve performance and durability and apply improvements to novel membranes.

Accomplishments

- Synthesis of 2,2-bis(*p*-hydroxyphenyl) pentafluoropropanesulfonic acid, a fluorinated bisphenolic comonomer devoid of aliphatic hydrogen atoms.
- Sulfonation of bis(4-chlorophenyl) sulfone.
- Generation of sPAES polymers using established synthetic sequences
- Changes in macromolecular relaxation and conduction processes in Nafion® membranes upon annealing at temperatures above 100°C were identified. Conclusions from this study are useful in explaining drop in performance of Nafion® in fuel cells at high temperatures.
- Discovered that membrane degradation severely reduces modulus, ductility and ability to withstand stress, as related to stresses generated from humidity and temperature changes in actual fuel cells.

Introduction

PEMFC research and development has been highly influenced by Nafion® membranes despite their shortcomings. Nafion®'s perfluorinated chemical

structure of renders it relatively resistant to chemical attack and beneficially increases the acidity of sulfonic acid groups. Although Nafion® remains the benchmark against which PEM performance is measured, it is expensive and exhibits undesirable mechanical durability. It suffers from a moderate glass transition temperature, which reduces mechanical durability during operation in a fuel cell; swelling - de-swelling upon RH cycling causes crack and pinhole formation leading to fuel crossover. Membrane performance suffers greatly around and above 100°C owing to dehydration. The objective is to engage in the fine molecular tailoring and evaluation of novel hydrocarbon membranes that overcome these problems in PEMFCs. This project aims to develop aromatic copolymers that should (1) exhibit enhanced chemical and mechanical durability over a broad temperature and humidity range, (2) have high proton conductivities at high temperatures and low humidity, and (3) be synthesized from readily available and inexpensive materials.

In this work we will characterize the synthesized novel membranes for structure, viscoelastic properties (and within the context of mechanical degradation), macromolecular chain dynamics, proton conductivity, accelerated ex and in situ degradation and fuel cell performance. To improve membrane durability, mechanical and barrier properties will be adjusted by polymer in situ sol gel processes for metal alkoxides.

Approach

To achieve these objectives, sPAES polymers will be synthesized using nucleophilic aromatic substitution to link successive aromatic moieties via oxidatively resistant groups *e.g.*, ether, carbonyl, sulfone, and hexafluoroisopropylidene. Copolymerization of sulfonic acid-containing monomers will be pursued in preference to post-polymerization sulfonation. To enhance the performance of known sPAES polymers used in PEMFCs, new bisphenolic comonomers containing ion-exchange moieties on a perfluorinated alkyl tether will also be synthesized.

Membrane chain dynamics, thermal transitions and conductivity aspects are explored using a broadband dielectric spectrometer with samples being tested between parallel plate electrodes. The real and imaginary components of the complex dielectric permittivity were determined over a range of frequencies and temperatures. Relaxation times and their distributions are extracted from the data. Viscoelastic/mechanical testing (stress-strain, creep, dynamic mechanical modes) is performed using a material test system device. Nafion® membranes are degraded under open circuit voltage conditions at 90°C, 30% RH for 45 and 72 h. A control Nafion® MEA was fabricated using Vulcan XC-72 carbon black and was subjected

to identical ink making and decal transfer process but was not assembled in a fuel cell. Some samples were degraded ex situ in Fenton's reagent.

Results

A bisphenolic comonomer, 2,2-bis(*p*-hydroxyphenyl)pentafluoropropanesulfonic acid, has been synthesized using hexafluoroacetone, sulfur trioxide, and phenol as building blocks. Hexafluoroacetone rapidly reacts with triethyl phosphite at -60°C to form the vinyl ether reagent, EtO(CF₃)C=CF₂ in good yields [1]. Fluoro-olefins are electron deficient and poor nucleophiles necessitating the use of liquid sulfur trioxide as a sulfonating agent. Addition of SO₃ to the vinyl ether reagent at -15°C creates a mixture of ethyl 2-ketopentafluoropropane sulfonate and the desired 2-ketopentafluoropropanesulfonic acid [2]. Conversion of the ester to the desired acid can be achieved via transesterification with excess trifluoroacetic acid. 2-ketopentafluoropropanesulfonic acid readily reacts with two equivalents of phenol to generate, 2,2-bis(*p*-hydroxyphenyl)pentafluoropropanesulfonic acid, which is isolated as a pyridinium or alkali metal salt [3]. This condensation reaction is self-catalyzed by the strong sulfonic acid reagent.

Synthesis of sPAES has continued for use in collecting benchmark data and to gain knowledge that will be applied to the synthesis of our novel copolymer. Recently a batch of sPAES was prepared and characterized by nuclear magnetic resonance to determine the percent sulfonation and the number average molecular weight. The percent sulfonation was determined to be 23.3% and the molecular weight was found to be 30,300 g mol⁻¹. The spectra also showed that a portion of the endgroups were composed of unreacted bisphenolic comonomer. This was attributed to addition of an insufficient amount of 3,3'-disulfonated 4,4'-dichlorodiphenyl sulfone monomer leading to unreacted phenolic endgroups in the copolymer.

Although reaction to form the sulfonated monomer has been successful, its isolation as a pure compound free of inorganic salts has been difficult, which in turn has caused difficulty in accurately charging the prescribed molar quantity into the polymerization reactor. Although the polymerization was slightly off-stoichiometric, the resulting polymer could be cast into tough films from a dimethyl acetamide solution.

Dielectric spectroscopy. Broadband dielectric spectroscopy (BDS) was used to investigate real time coupling between macromolecular motions and the proton conduction process in Nafion® membranes during annealing at temperatures above 100°C in the instrument. These studies will set the stage and provide benchmark data for similar investigations of our novel hydrocarbon membranes.

In Figure 1 are α and β relaxation time (τ) shifts with annealing time (t) at 140°C. This high temperature was chosen so that the α transition is on-scale. The β relaxation is attributed to long range backbone motions within an electrostatic network and the α relaxation involves the same but as influenced by disruption of polar aggregates that become dynamic [4]. The increase in each τ with increasing t indicates slower motions attributed to progressive water loss that decreases free volume. Polar domains dehydrate faster as seen in the more rapid increase in τ_α and the lesser increase in τ_β is rationalized in terms of the Yeager-Steck view of mixed interphases in which water is incorporated to a degree [5]. It would be important to determine relaxation times for both relaxations for annealing at other temperatures >100°C to compare the activation energies of each.

A parameter N , a coarse degree of connectivity of proton pathway networks, was derived and its behavior with regard to annealing time and relationship to conductivity was determined.

BDS was used to study chemical degradation (in Fenton reagent) on chain motions and meaningful correlations were established; degraded membranes showed a split in the β relaxation which might reflect chains with different lengths.

Mechanical properties of degraded MEAs. Tensile properties at 80°C and 100% RH were measured by stretching control and degraded MEAs at 5 mm/min. Stress-at-break for 45 and 72 h degraded MEAs is 6 and 9 times lower while strain-at-break is 24 and 28 times lower, respectively, than that of the control. Modulus reduction due to decrease in molecular weight resulting from suggests that the membrane can easily deform under stress and rupture and pathways for fuel crossover – that leads to radical attack – can form. Figure 2 shows scanning electron microscope (SEM) images of control and degraded MEAs subjected to 10 MPa creep for 3 h

FIGURE 1. Nafion® β and α Relaxation Times vs. Time of Annealing at 140°C

FIGURE 2. SEM Micrographs of Surfaces of (A) Control, (B) 48 h Degraded and (C) 72 h Degraded Nafion® MEAs After Creep Tests

at 80°C. Degraded MEAs developed cracks in response to applied stress. Cracks for 72 h degraded are wider than those for 45 h degraded MEAs due to reduced ductility of the former. No huge cracks were observed for the control although there was crazing associated with large scale deformation.

Conclusions and Future Directions

- Continue our synthetic strategies concerning development of new bisphenolic comonomers containing ion-exchange moieties attached to perfluoroalkyl tethers. Optimization of the synthesis of 2,2-bis(*p*-hydroxyphenyl) pentafluoropropanesulfonic acid will allow for use of this comonomer in polymerization reactions to create new sPAES polymers for fuel cell membranes. Additionally, we envision employing similar chemical methods described above to create a library of analogous compounds.
- BDS revealed macromolecular dynamics and nature of proton hopping pathways vs. time of annealing Nafion® at a high temperature above the α transition.
- BDS also revealed shifts in macromolecular dynamics in chemically degraded Nafion®.
- Preliminary mechanical deformation studies of Nafion® MEAs suggest significant deterioration in structure and properties over time in a fuel cell.
- Future directions include, for novel membrane materials: (1) BDS characterization of macromolecular motions and thermal transitions in the context of high T_g , high temperature fuel cells; and (2) BDS in situ real time investigations of membrane annealing and drying processes as related to equilibrium morphology attainment and high temperature stability and water retention. Viscoelastic investigations of the novel synthesized membranes will be conducted as related to mechanical durability in RH cycling in fuel cells.
- Membranes will be inorganically modified by the in situ sol-gel technique for metal alkoxides and the effect of these modifications on membrane performance and durability will be investigated.

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V.E.1 Advanced Cathode Catalysts and Supports for PEM Fuel Cells

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Projected End Date: March 31, 2011

- high prospects for 40,000 hours durability under operating conditions for stationary applications, and
- high volume manufacturability.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan (HFCIT MYRDDP):

- (A) Durability
- (B) Cost
- (C) Performance
- (D) Water Transport Within the Stack

Technical Targets

This project is focused on improving the performance and durability of the 3M nanostructured thin film catalyst (NSTF) roll-good fabricated electrocatalysts and MEAs. Table 1 compares the NSTF current 2nd quarter, calendar year (CY) 2009 status with the electrocatalyst targets for 2010/2015 from Table 3.4.12 of the DOE HFCIT MYRDDP. Additional rows were added to summarize recent accelerated durability test results. All metrics were obtained with the same cathode and anode alloy catalysts. The MEAs used for the inverse specific power density values listed in the first row, PGM total content, had loadings of 0.05/0.10 mg_{Pt}/cm² on the anode and cathode, respectively. The short stack results were obtained outside the project but evaluated catalysts and gas diffusion layer (GDL) developed within the project.

Accomplishments

- Improved baseline NSTF-MEA roll-good performance containing 0.15 mg-Pt/cm² total loading (0.1 cathode) to obtain 0.62 V at 1.5 A/cm² under 150 kPa H₂/air inlet pressure at 80°C, 67% relative humidity (RH). Performance reproduced in 50 cm² single cell measurements at General Motors.
- Demonstrated inverse specific power density in a 50 cm² cell that exceeds the DOE 2015 target of 0.20 g_{Pt}/kW at 650 mV. Similar value obtained by system integrator in a short stack with same 0.05/0.10 mg_{Pt}/cm² loadings.
- Demonstrated a 50% increase in oxygen reduction reaction (ORR) mass activity, from 0.18 to 0.27 A/mg_{Pt}, using the DOE protocol for activity at 900 mV, with a new PtM alloy over our standard Pt₆₈(CoMn)₃₂.

Objectives

The objectives of this project are development of a durable, low-cost (both precious group metal [PGM] content and manufacturability), high performance cathode electrode (catalyst and support), which is fully integrated into a proton exchange membrane electrode assembly (MEA) characterized by:

- total Pt group metal loading per MEA of ≤ 0.25 mg/cm²,
- short-stack specific power density of ≤ 0.3 g/kW at rated power,
- durability sufficient to operate at $>80^\circ\text{C}$ for 2,000 hours, $\leq 80^\circ\text{C}$ for 5,000 hours, with cycling for transportation applications,

TABLE 1. Progress towards Meeting Technical Targets for Electrocatalysts and MEAs for Transportation Applications

Characteristic	Units	Targets 2010/2015	3M Status – 6/09 (mfg'd roll-good)
PGM Total Content	$\text{g}_{\text{Pt}}/\text{kW}_e$ rated in stack	0.3/0.2	<0.18$\text{g}_{\text{Pt}}/\text{kW}$ for cell $V < 0.67$ volts in 50 cm^2 cell at 150 kPa inlet. 0.19$\text{g}_{\text{Pt}}/\text{kW}$, 400 cm^2 short stack
PGM Total Loading	mg PGM/ cm^2 total	0.3/0.2	0.15 with current PtCoMn alloy
Durability under Load Cycling	Hours, $T \leq 80^\circ\text{C}$ Hours, $T > 80^\circ\text{C}$	5,000 / 5,000 2,000 / 5,000	>7,000 hours , 0.2/0.2 mg/cm^2 , mech. reinforcement, no chem. stab. , ~ 5,000 hours , 0.05/0.1 mg/cm^2 , no chem. stab. or reinforcement
Mass Activity (150 kPa H_2/O_2 , 80°C, 100% RH)	A/mg-Pt @ 900 mV, 150 kPa O_2	0.44 / 0.44	0.18 A/mg in 50 cm^2 w/ PtCoMn 0.27 $\pm$ 0.04 A/mg in 50 cm^2 with Pt _x M _y , both 0.1 $\text{mg}_{\text{Pt}}/\text{cm}^2$ on cathode.
Specific Activity (150 kPa H_2/O_2 at 80°C, 100% RH)	mA/cm^2 -Pt @ 900 mV	0.72 / 0.72	1.7 for PtCoMn, 0.1 $\text{mg}_{\text{Pt}}/\text{cm}^2$ 2.1 $\pm$ 0.3 for new Pt _x M _y , 0.1 $\text{mg}_{\text{Pt}}/\text{cm}^2$
Accel. Loss: 30,000 cycles, 0.7–0.9 V step, 30 sec hold at 80/80/80°C	-mV at 0.8 A/ cm^2 %ECSA loss	<30 mV <40% / 40%	~ 0 mV loss at 0.8 A/ cm^2 ~ 0 % loss of $\text{cm}^2_{\text{Pt}} / \text{cm}^2_{\text{planar}}$
Accel. Loss: 200 hr hold @ 1.2 V at 95°C, H_2/N_2 , 150 kPa, 80% RH	-mV at 1.5 A/ cm^2 % ECSA loss	<30 mV <40% / 40%	+ 25 mV gain at 1.5 A/ cm^2 ~ -17% loss of $\text{cm}^2_{\text{Pt}} / \text{cm}^2_{\text{planar}}$
OCV hold without PEM failure under 250/200 kPa H_2 /air, 90°C, 30% RH and periodic stops for ECSA, x-over meas.	Hours mA/cm^2	200 <20	950 to 1,340 Hrs. H_2 Crossover <20 mA/cm^2 , F-ion release rate < 0.5 $\mu\text{g}/\text{cm}^2\text{-day}$
Accel. Loss: 4,000 cycles 0.6–1.2 V, 20 mV/sec, 95/95/95°C, 270 kPa, H_2/N_2	Specific Activity % ECSA loss	Not specified	-1% to + 5% gain in $\text{mA}/\text{cm}^2_{\text{Pt}}$ -25 + 5% loss of $\text{cm}^2_{\text{Pt}} / \text{cm}^2_{\text{planar}}$ with 0.05/0.10 $\text{mg}_{\text{Pt}}/\text{cm}^2$ on anode/cathode

RH – relative humidity; ECSA – electrochemically active surface area; OCV – open-circuit voltage; T - temperature

- Using rotating disk electrode (RDE) measurements on the new NSTF PtM alloy, demonstrated the highest ORR specific activity, mass activity and half-wave potential values for any catalyst to date: i_{kin} at 0.90 V = 6.8 mA/cm^2 -Pt, 1.1 A/mg-Pt, and $E_{1/2}$ = 0.962 V, with 0.10 $\text{mg}_{\text{Pt}}/\text{cm}^2$ loading on the NSTF whiskers.
- Completed three designed experiments on production equipment to correlate whisker-support surface area with process conditions, that allowed development of a quantitative model of catalyst surface area and the understanding of how it depends on the whisker characteristics and growth conditions.
- Exceeded by a factor of five the 2015 OCV hold lifetime targets at 90°C (250/200 kPa H_2 /air, and 30% RH) while cross-over remained below 20 mA/cm^2 and F⁻ ion release rates remained below 0.50 $\mu\text{g}/\text{cm}^2\text{-day}$.
- Repeated over 7,000-hour lifetime under humidity load cycling lifetime tests at 80/64/64°C, (cell temperature/anode dew point/cathode dew point) with a second MEA having no ionomer chemical additives, but mechanical stabilization as reported in the CY 2008 report.
- Demonstrated 5,000-hour lifetimes of two MEAs with the same humidity load cycling lifetime test as above, but using the current “best of class” NSTF catalyst-coated membrane (CCM) having 0.05/0.10 mg/cm^2 PtCoMn on the anode and cathode, respectively, and a 20 micron thick 3M 850 equivalent weight (EW) membrane that did not contain chemical additives or mechanical reinforcement.
- Demonstrated 0 to 5% gain in specific activity and -20% to -30% loss in surface area with 0.10 mgPt/cm^2 cathode loading under 0.6 to 1.2 volt cyclic voltammetry (CV) cycling at 20 mV/sec under more severe conditions of 95/95/95°C (cell/dew point temperatures).
- Produced over 55,000 linear ft combined of NSTF substrate, coated catalyst, and CCM for process development, qualification and use (partially produced for the current contract).
- Identified critical protocol and materials factors having significant effects on the break-in conditioning requirements for the low loading NSTF MEAs, and initiated a new task to focus on this issue. Developed a simplified air cooling, voltage cycling protocol for conditioning that reduced break-in time from over 24 hours to less than 6 hours.
- Quantified new transient power-up issues with NSTF thin layer electrodes and established a

protocol to study them. Identified new MEA interface and GDL concepts for addressing both transient and steady-state flooding under cool wet conditions characteristic of ultra-thin electrodes.

Introduction

State-of-the-art proton exchange membrane (PEM) fuel cell electrocatalyst technology utilized in today's prototype fuel cell vehicles are demonstrating significant limitations with respect to general durability and robustness under start-stop cycling, adequate performance with low PGM loadings, and low-cost manufacturability. To a large degree, these deficiencies are traceable to properties of the conventional carbon supported dispersed Pt catalysts in use today. The research and development of this contract are focused on overcoming these three most critical barriers for fuel cell MEA automotive deployment by using an alternative catalyst support and deposition method.

Approach

The approach for attaining the above objectives builds on a 12-year DOE/3M funded development of the 3M NSTF catalyst and MEA technology. The NSTF catalyst fundamentally has higher specific activity for oxygen reduction [1,2], removes all durability issues with carbon supports while demonstrating much lower losses due to Pt dissolution and membrane chemical attack [3,4,5,6], and has significant high volume all-dry roll-good manufacturing advantages [7].

The scope of work in the first two-year budget period included extensive work at 3M to increase the NSTF catalyst support film surface area, fabrication and screening of new alloys in 50 cm² single cells, and evaluation of multiple deposition parameters to obtain increased catalyst surface area and utilization. Complementary to this work at 3M, collaborative work included high throughput fabrication and characterization of new multi-element Pt alloys (ternaries and quaternaries) with Dalhousie University, fundamental catalyst characterization studies with ANL, and development and evaluation of a pseudo-RDE catalyst evaluation technique with JPL. Research in the second year has continued to focus on development and characterization of GDL materials and process methods for improved cool-start and water management of the ultra-thin NSTF electrodes; application of various accelerated aging tests for membrane and catalyst durability and lifetime improvement; and catalyst/membrane integration for improved CCM performance with reduced Pt loading.

Results

The technical accomplishments for the first year fall into six areas of research and development corresponding to Project Tasks 1.1, 1.2, 1.3, 2, 5.1, 5.2 and 6. We briefly summarize the main results from each of these areas.

In the first area (Task 5.1), the improvements in catalyst electrodes, membrane and GDL are combined to establish a current "best of class" MEA. Similar to last year, we further improved high current density performance while reducing the total Pt loading. At the start of the contract, our baseline CCM consisted of the NSTF PtCoMn ternary at a loading of 0.2 mg-Pt/cm² on both the anode and cathode sides of a 3M PEM (~35 microns, 850 EW). Last year we reduced the size of the microstructure features of the NSTF roll-good substrate, which improved mass transport to the catalyst at high current densities, and reduced the anode and cathode loadings to 0.1 and 0.15 mg/cm², respectively. This year, we further reduced the PtCoMn catalyst loadings to 0.05 and 0.10 mg/cm², respectively, and the membrane thickness from 32 to 20 µm with a subsequent gain in performance. Figure 1(a) illustrates galvanodynamic polarization curves under 150 kPa H₂/air from the current best of class NSTF MEAs compared to last year's status, showing a 34% reduction in impedance and an 85 mV gain at 2 A/cm² while using 40% less Pt. Figure 1(b) shows the same curves from (a) plotted as inverse specific power density versus cell voltage, indicating the new results now exceed the DOE 2015 target for this metric in the peak power range. Tafel plots of the galvanodynamic scan (GDS) polarization curves from 1(a) show a 70 mV/decade slope and an ~40% reduction of the mass transport overpotential at 2 A/cm² with the new MEA constructions over last year's.

The second results area was that of Task 1.1. This is a major task focused on increasing the surface area of the NSTF whisker supported catalyst. There are two aspects to increasing the surface area, viz. increasing the surface area of the bare whisker support and increasing the surface area of the thin film catalyst coating applied to the whiskers. All the work under this task has been done with the standard NSTF PtCoMn ternary catalyst. The primary emphasis of the work at 3M in the past year has centered on completing three designed experiments conducted on pilot-scale facilities to produce NSTF whisker support particles with controlled physical characteristics of areal number density, N, whisker length, L, and diameter, d. The first of these designed experiments was introduced in last year's report and completed by the end of CY 2008. Whiskers were fabricated under 24 different process condition parameter sets using the roll-good manufacturing equipment. Two subsequent whisker area optimization experiments built on the knowledge gained from the

FIGURE 1. (a) Galvanodynamic polarization curves under 150 kPa H₂/air from the current best of class NSTF MEAs compared to last year's status, showing a 34% reduction in impedance and an 85 mV gain at 2 A/cm² while using 40% less Pt. (b) The curves from (a) plotted as inverse specific power density versus cell voltage showing the DOE 2015 target is now exceeded by the current best of class NSTF MEA.

first. A primary outcome of these experiments has been the first understanding of how the measured ECSA, from H_{upd} measurements, is related to the physical characteristics of the whisker support film, the catalyst loading, and the whisker growth process conditions. This has permitted development of a quantitative model of Pt surface area as a function of the whiskers' dimensions and number density, the mass loading and alloy density, the fraction α of catalyst coated onto the sides of the whiskers, and a scaling parameter f for the catalyst coating roughness factor. Using the model and generic values for the latter two parameters, α and f , deduced from five whisker support types, the resultant mass activity could be calculated as a function of N^*L and the specific activity. This was then used to project that a 67% gain in N^*L and a 50% gain in specific activity would be sufficient to meet the DOE 2015 targets for mass activity at 900 mV of 0.44 A/mg_{Pt}.

The whisker support area and the subsequent catalyst coating surface area contribute to the total surface area and are related. The understanding of how they are related is a second primary outcome of this task. The structural model for the thin film catalyst coating on the whiskers is that of the NSTF "whiskerettes" that grow epitaxially off the side planes of the crystalline whiskers [8]. From the results of the Task 1.1 work this year, we have determined that for a given alloy composition and loading, the catalyst thin film grain size (whiskerette size) and ratio of exposed Pt face-centered cubic (hkl) crystal facets (from X-ray diffraction) determine the catalyst's activity, how it varies with loading and how it depends on the support whisker surface area. The second and third whisker area optimization experiments have continued to increase our knowledge of how to obtain the required surface area increase of the whisker supports and catalyst thin film over-coating for a given loading. No substantial increase in specific surface area at the 0.1 mg/cm² loadings above 10 m²/g has been achieved in the past year, but work is continuing with two remaining whisker-growth process parameters that have not previously been investigated.

In the third results area (Tasks 1.2 and 1.3) the focus was on development of new Pt alloys to increase specific activity and durability, independent of the whisker support surface area development work of Task 1.1 discussed above. For all this work with new alloys, the standard NSTF whisker support was used and 50 cm² single cells were used. The objective is to increase the absolute and mass activities above that obtained with the standard PtCoMn. Two activity criteria that must be met are illustrated in Figure 2(a), which shows the absolute ORR activity at 900 mV plotted versus cathode mass activity. The DOE targets for 2015 are indicated. The results for standard PtCoMn on many different whisker structures investigated in Task 1.1 at loadings of 0.05, 0.1, 0.15 and 0.2 mg_{Pt}/cm² are shown as the black squares (0.2), red circles (0.15), and purple triangles (0.05 mg/cm²). The Task 1.1 results for the 0.1 loadings are hidden under the much larger series of new catalyst alloys (blue squares) studied at 0.10 mg/cm² loadings under this Task 1.3. As seen, the new alloy work has been successful in getting much closer to the DOE targets, and the loading of 0.1 mg/cm² appears to be the shortest path. For the activity measurements in Figure 2(a), the DOE protocol at 900 mV under saturated 150 kPa H₂/O₂ is used, in which the current density is taken 1,050 seconds after setting the cell potential at 900 mV, having been held at ~0.10 V under N₂ for 20 min. During this time, the Pt surface is oxidizing and the current degrades as the state of the surface changes. This raises the question of whether this is a reliable protocol to compare different alloy systems that can oxidize at different rates. Figure 2(b) shows the ORR absolute activity recorded at nominally 5 seconds after setting the potential at 900 mV versus that at 1,050 seconds,

FIGURE 2. (a) Plot of absolute activity versus mass activity at 900 mV for a large series of NSTF catalysts alloys, loadings and whisker support types investigated during the past year, relative to the DOE targets. (b) Absolute ORR activity for a series of different NSTF alloy catalysts, measured in 50 cm² cells at 5 seconds after setting the cell potential at 900 mV versus the value at 1,050 seconds after setting the cell potential at 900 mV.

for a wide series of the NSTF alloy compositions and loadings investigated in 50 cm² cells. Three things are apparent in Figure 2(b). First there is significant scatter, indicating different decay rates for different alloys and compositions. Second, the ORR values at 5 seconds are roughly twice the values obtained at 1,050 seconds, and most meet or exceed the DOE target values of 44 mA/cm²_{planar}. The ORR activity values at 5 seconds are indicative of the clean surface state, and therefore comparative to RDE measurements in which the catalyst is acid washed and due to the CV scan rates and directions, also representative of the clean surface state. Third, the new PtM compositions (red squares in

Figure 2(b)) are by far the most active and exceed those of PtCoMn at the standard composition.

Figure 3(a) shows the mass activity (1,050 sec values) versus platinum loading for the standard NSTF PtCoMn composition and the new PtM alloy at the preferred composition. PtM shows a statistically significant gain in mass activity by ~50% at the 0.10 mg/cm² loading. The commensurate kinetic performance improvement in fuel cell polarization curves is also obtained with the new PtM catalyst. However, high kinetic activity is only one necessary performance criterion for a suitable electrocatalyst, and the new PtM catalyst is not ready yet to replace the PtCoMn. We are actively working on the issues it presents for high current density and durability. This involves optimization of post fabrication process steps that have been found productive.

In Figure 3(b) we show the mass activity measured at 5 seconds versus the Pt loading for the preferred PtM composition. The 3M values in 50 cm² single cells are plotted as red stars. For comparison we show the mean values of multiple sample measurements for the same catalyst lots made by RDE at ANL (blue squares). What is remarkable is that the 50 cm² and RDE values agree quantitatively fairly well with no adjustable parameters, consistent with the point discussed above that the 5 sec fuel cell measurement is more representative of the clean surface state, as in RDE measurements. The RDE measurements are optimized for the amount of NSTF catalyst particles applied to the glassy carbon disks. By these metrics then, activity measured on the clean surface state in a fuel cell at 900 mV or by RDE, the PtM alloy activity significantly exceeds the DOE target, and in fact, the standard PtCoMn catalyst activity also meets the target. The good correlation of the RDE and fuel cell (at 5 sec) activity measurements has also been demonstrated for a series of other alloys, including PtCo, PtNiFe, PtCoMn, PtCoNi and PtCoZr.

Another important outcome of this Task 1.2 work with ANL has been the successful demonstration of a post-fabrication catalyst treatment that in RDE measurements increases the mass activity by 60% over the as-received alloys. This has been born out for PtM, PtCoMn, PtNiFe, but not for pure Pt. It is believed that the surface structure composition is being affected by the post treatment. Work completed at 3M has also involved experiments to duplicate the post-fabrication treatment and identify a roll-good compatible process.

The third area of results includes all the work done with Dalhousie University to develop new catalyst compositions and structures using high-throughput compositional spread screening methods [5]. Samples comprising sixty-four electrode arrays of thin film catalysts deposited onto the NSTF whisker supports are prepared at Dalhousie University, converted into MEAs

FIGURE 3. (a) Plot of mass activity versus Pt loading for the new PtM alloy and the NSTF standard PtCoMn composition, measured in 50 cm^2 cells. (b) Mass activity at 900 mV versus Pt loading on the NSTF whiskers for the new NSTF PtM alloy composition, measured at 3M in multiple 50 cm^2 cells with the 5 sec protocol (red stars), compared to the values from ANL by RDE at 900 mV.

at 3M and evaluated in 64-channel cells at Dalhousie. Initial results were summarized in Figure 4 of last year's annual progress report. Over 70 additional libraries were fabricated and tested this year, involving many different binary, ternary and quaternary material sets (over 130 to date). Extensive surface area measurements in the 64 channel cells have been correlated with the lattice parameters and grain sizes of the alloys as a function of composition. This work has led to a new patent application. The durability under high voltage CV cycling from 0.6 to 1.2 V has been determined for most libraries and continues to be a key method to survey new alloy resistance to Pt dissolution. A new methodology for doing rotating ring disc electrode tests on NSTF whiskers grown directly on glassy carbon disks has also been developed and appears to be an excellent method with very high signal to noise for studying low catalyst loadings. With this approach and the newest

FIGURE 4. Examples from three types of accelerated durability testing: (a) GDS polarization curves from the best of class MEA before, during and after 30,000 cycles from 0.7 to 0.9 V (30 sec hold, square wave) under 7.35 psig H_2/N_2 and 80°C cell and dew point temperatures. (b) OCV hold test versus time with periodic measurements of crossover and F^- ion release for two NSTF MEAs that contained a chemical stabilizer in the 20 μm 3M PEM. (c) Open circuit voltage versus time under an 80°C cell temperature, 64°C DP, load cycling protocol for two best of class MEAs containing the 0.05/0.10 mg/cm^2 loadings, a 20 μm thick 850 EW 3M PEM with neither chemical stabilizers nor mechanical reinforcement. Both achieved 5,000 hours before OCV dropped below 0.8 V.

NSTF alloys, Dalhousie is observing surface areas as high as 30 m^2/g_{Pt} and kinetic currents so high that 1.0 V is being used to fully eliminate transport effects.

This area also includes work completed with JPL to generate and screen new NSTF alloy catalysts deposited at JPL onto multi-electrode arrays of NSTF whiskers. These are then characterized both ex situ and in a novel JPL electrochemical cell with rotating electrolyte that simulates an RDE measurement. The equipment and techniques for depositing the thin film catalysts onto the NSTF support whiskers were fully implemented to fabricate 18 electrode arrays, and characterization in the novel pseudo-RDE cell was completed for several binary and ternary alloy systems at JPL. Comparison experiments to obtain the equivalent rotating disc speed of the JPL approach have been made and suggest that the equivalent RDE speed of the circulating electrolyte approach may be insufficient for in situ ORR characterization. Increased focus on catalyst alloy fabrication by two methods unique to JPL's facilities is being pursued.

In the fourth results area (Task 2) we continued to carry out five types of accelerated durability tests using both the NSTF baseline MEA from the start of the contract and the reduced loading, thinner membrane MEAs, discussed in Figure 1.

Test 1 was a 30,000 cycle, 0.7 V (30 sec hold) to 0.9 V (30 sec hold) step-wise cycling test at 80°C and saturated conditions under 7.35 psig H_2/N_2 , with periodic interruptions for measuring catalyst surface area, activity and MEA performance. This test evaluates resistance to Pt dissolution. The target value for surface area loss was <40% and for mass activity <60% (measured at 900 mV, 150 kPa saturated H_2/O_2). Test results were discussed in last year's report for the 2008 best of class MEA with the 0.1/0.15 mg/cm² catalyst loadings, for which those NSTF MEAs demonstrated 0% loss in ECSA, a mass activity loss of ~13%, and a performance gain of 2 mV at 0.8 A/cm². This gain in performance was observed at all current densities and increased with current density and after each new measurement. After 30,000 cycles, the gain in potential at 1.5 A/cm² was 19 mV. The NSTF electrodes appear to be completely stable under this accelerated test. This year the same test was applied to the 2009 best of class MEA discussed in Figure 1, with the 0.05/0.10 mg/cm² loadings and thinner PEM. A series of the DOE test protocol-required GDS polarization curves (25 psig, 80°C, 64% RH) are shown in Figure 4(a) after 0, 1K, 5K, 10K, and 30K cycles. The polarization curves increase uniformly from 0K to 10K cycles, and then show some loss between 10K and 30K cycles relative to the initial, 0K curve. At 0.8 A/cm², the overall loss was about 10 mV after the 30K cycles. The ECSA loss after 30K cycles was -22% for each of two MEAs. Both performance and ECSA loss for the new NSTF baseline MEA with 0.05/0.10 mg_{Pt}/cm² after the 30K cycles exceeds the DOE 2015 target but are worse than was measured for the 2008 baseline reported last year, for

which no loss of performance or ECSA was obtained (as still listed in Table I as the best result for this test).

Test 2 is a lifetime-hold at OCV at 90°C under 250/200 kPa H_2 /air at 30% RH. This test evaluates MEA chemical stability. Figure 2 of last year's report showed a test result in which the NSTF MEA used had the NSTF PtCoMn ternary catalyst (0.2 mg-Pt/cm²) on both anode and cathode sides of a neat (no chemical additives, or reinforced) 3M 850 EW, 35 micron thick PEM. Although the DOE test target time of 200 hours was exceeded by about a factor of four, when it was attempted to do periodic shut-downs to measure cross-over as a function of time, the MEAs typically failed. This year, we show in Figure 4(b) the results from two MEAs that had the lower anode/cathode loadings of the 2008 baseline MEA, and a 3M 850 EW 20 µm PEM that contained chemical stabilizers. As shown the MEAs were successfully operated for 900 and 1,300 hours respectively with periodic shutdowns for cross-over and F⁻ ion release rates. The cross-over remained below 20 mA/cm² and F⁻ ion release rates remained below 0.50 µg/cm²/day over their lifetimes.

Test 3 is a load cycling test, results of which were reported last year in Figure 3 of the Fiscal Year 2008 annual progress report. Cell voltages at various current densities are measured versus time under an 80°C cell temperature, 64°C dew point, constant flow load cycling protocol. OCVs (measured daily) were compared for both NSTF and conventional dispersed Pt/C based MEAs. NSTF MEAs with 0.2/0.2 mg_{Pt}/cm² loadings on 3M 35 µm membranes containing neither chemical stabilizer nor reinforcement had mean lifetimes of ~3,500 hours, ~seven-fold longer than the conventional MEAs with the same membrane and GDL. However, when the NSTF electrodes were applied to an experimental membrane containing the same 3M ionomer that was reinforced courtesy of W.L. Gore, the lifetime exceeded 7,000 hours. In the past year, a second identical MEA also exceeded 7,000 hours prior to its OCV dropping consistently below 0.8 V (the criterion for end of life). But this year we also evaluated the current best of class NSTF CCM with the 0.05/0.10 mg/cm²_{Pt} loadings on a 3M 850 EW PEM that did not contain any chemical stabilizer or mechanical reinforcement. Under the same load cycling test protocol, the first two MEAs evaluated had lifetimes of approximately 5,000 hours before their OCV dropped consistently below 0.8V, as shown in Figure 4(c). Although this just barely meets the DOE 2015 target goal, combining the lower loading electrodes with a 3M PEM having chemical additives should be able to significantly exceed the DOE targets, (re: 3M Membrane project DE-FG36-07GO17006).

Tests 4 and 5 are high voltage cycling tests to test for Pt dissolution. In both tests the cathode under N_2 is cycled (relative to the anode under H_2) 4,000 times between 0.6 and 1.2 V at 20 mV/sec at temperature and

100% inlet RH. For Test 4, $T = 80^{\circ}\text{C}$, $P = 0$ psig while for Test 5, the cell temperature and dew points were 95°C and pressures were 14.7 psig. Under Test 4, the current best of class MEAs, with the $0.05/0.10 \text{ mg}_{\text{Pt}}/\text{cm}^2$ on the thinner 3M PEM, experienced ~ 10 mV loss uniformly from 0.2 to $1.6 \text{ A}/\text{cm}^2$, -15 to -17% loss in ECSA, and minimal mass transport loss. At the more severe Test 5 conditions, the same MEAs exhibited 20 to 30% ECSA gain after 4,000 cycles, 10-21 mV of kinetic performance and some increased mass transport losses relative to the Test 4. Although there are no designated DOE targets for these tests, each of these results are no worse than were previously obtained with the higher loaded 2008 baseline NSTF MEAs, but represent an opportunity for further improvement.

The fifth area of work (Task 5.2) focused on development of GDL materials and process parameters, and fuel cell test protocols for improved water management with the ultra-thin NSTF type electrodes. Water management properties are different for the NSTF electrodes which are 20-30 times thinner than conventional dispersed catalyst electrodes. This is particularly noticeable for operation under cold-wet conditions since the rate of water generation per unit of catalyst surface area is roughly six times higher for the lower surface area/loading NSTF electrodes. This correlates very well with measured limiting currents. For example, using standard hydrophobic GDLs at 30°C the current density at 0.6 V for an NSTF cathode with $0.1 \text{ mg}_{\text{Pt}}/\text{cm}^2$ is roughly five to six times lower than for a conventional Pt/C electrode with $0.4 \text{ mg}_{\text{Pt}}/\text{cm}^2$. This means that under cool, wet steady-state conditions, liquid water must be moved to compensate for the reduced vapor transport mechanism, while for fast dynamic low-to-high power transient events, sufficient surface area or volume must be available to accommodate the water of generation for the few seconds it takes for electrode heating to enable vapor transport.

Conventional GDLs are not designed to move liquid water. Modified GDL materials and electrode interfaces with the GDL and membrane are likely required to enable adequate water transport under all conditions for ultra-thin, low loading electrodes. This year three designed experiments were fully completed around the current best practices GDL carbon paper backing layer, microporous layer modifications and GDL processing. The first of these were initiated last year and included the type of carbon paper used for the electrode backing, percent and type of fluoropolymer used for wet proofing, the microporous layer coating weight and drying conditions, type and amount of fluoropolymer used in the MPL, different approaches for incorporation of hydrophilic materials into the GDL, and asymmetric anode/cathode GDLs. These experiments defined the envelope of possibility with essentially conventional all-hydrophobic GDL structures, to meet cool and

wet as well as hot and dry operating condition. No combination of GDL materials and processing were found to substantially improve the cool, wet operation over the current best practices 3M GDL. Some modest improvements were demonstrated in short stack tests with GDLs having modified MPL materials, and avenues along those material sets are being pursued. Perhaps more promising, modified electrode structures and interfaces have very recently been shown to have a substantial benefit for transient response, and this work is accelerating to define the optimum type of interface capable of satisfying low temperature as well as high temperature conditions. Finally, non-conventional GDL physical structures are being developed and evaluated for direct liquid water transport under cool, wet conditions.

Finally, the sixth and last area of work is focused on improving break-in conditioning of the NSTF MEAs. This activity has now been incorporated as a new Task 6. Significant work prior to the current project has identified many MEA component materials and their processes, and test station protocols that strongly affect the time for break-in conditioning of new MEAs. These include catalyst composition, surface area, fabrication conditions, membrane processing solvents and drying conditions, and GDL types. A thermal cycling protocol with liquid water injection has been used for years to break-in new NSTF MEAs to obtain full performance. The new task is focused on both materials effects and the protocol effects in order to significantly reduce the time and simplify the procedures for conditioning a new MEA. At this time the new test station protocol work has been successful in reducing the conditioning time with our current test stations from over 24 hours to less than six hours. From a materials perspective, we have identified catalyst alloy effects that can increase the time for break-in conditioning by nearly two orders of magnitude and post fabrication processes that can reduce that time by even more for those catalysts. There are many parameters and effects that interplay in bringing an MEA to full performance as quickly as possible and this work will continue to be a focus to target a three hour break-in conditioning time with simplified procedures for the best of class MEA materials.

Conclusions and Future Directions

The project has met or exceeded all of the currently specified DOE electrocatalyst and MEA performance and durability targets for 2015 using the same MEA components, except for mass activity measured in a fuel cell at 900 mV by the DOE recommended protocol. If mass activity is measured from the non-oxidized catalyst surface by either RDE or in a fuel cell using a modified DOE protocol (5 sec vs 1,050 sec), then this target for 2015 has been met as well for the NSTF PtCoMn

catalyst. Further improvements in activity with new alloys and durability should be possible and work will continue in this direction. The project has increased its focus on understanding and improving the key water management issues associated with the NSTF electrodes, and simplifying and reducing the break-in conditioning time. Future work will be strongly focused on reducing these remaining gaps for a robust, durable, high performance, roll-good manufactured MEA containing no more than 0.15 mg/cm² of PGM combined on the anode and cathode.

Water Management Improvement

- Tailor the GDL materials and physical construction for more effective electrode water transport over a wide range of operating conditions without compromising high temperature performance under dry conditions.
- Develop MEA interface improvements to improve transient response and sensitivity to operating conditions.

Start-Up Conditioning (New Task)

- Continue to develop break-in conditioning protocols and catalyst/membrane components to reduce MEA break-in conditioning time to <3 hours for the best of class MEAs.

Cathode Catalyst Mass Activity Gain

- Continue to fabricate and test new catalyst compositions and surface structures to exceed the target mass activity at 900 mV of 0.44 A/mg_{Pt} using the standard (1,050 sec) fuel cell protocol and which meet all other performance and durability requirements.
- Achieve 50% gain in surface area of NSTF supports over current NSTF baseline without loss of specific activity or durability under the most severe accelerated test.

Durability Improvement

- Reduce by 50% any losses in surface area, activity or mass transport over-potential under the more severe fast high voltage cycling protocol (e.g. 4,000 cycles, 0.6–1.2 V under H₂/N₂ at 20 mV/sec at 95/95/95°C).

FY 2009 Publications/Presentations

1. Arman Bonakdarpour, Tara R. Dahn, Radoslav Atanasoski, Mark K. Debe, and Jeff R. Dahn, "H₂O₂ Release During Oxygen Reduction Reaction on Pt Nano Particles," *Electrochemical and Solid-State Letters*, **11**, B208-B211, 2008.

2. Radoslav Atanasoski and Mark Debe: "Nano-Structured Thin Film - NSTF Catalysts for PEM Fuel Cells: Fundamentals and Application" ACES Electromaterials Symposium "Nanostructured Electromaterials", University of Wollongong, NSW, Australia, 4-6 February 2009, *invited*.

3. Radoslav Atanasoski: "Fuel Cell Catalysts of Tomorrow": XX Congress of Chemist and Technologist of Macedonia Ohrid, Macedonia, September 16–21, 2008, *invited*.

4. Radoslav Atanasoski, Mark Debe and Tom Wood: "High performance platinum and non-precious metal catalysts for PEM fuel cell application" (NMES08-57), New Materials for Electrochemical Systems Symposium, Montreal, Canada, June 24–27, 2008, *invited*.

5. G. Vernstrom, A. Schmoeckel, R. Atanasoski, S. Hendricks, A. Steinbach, and M. Debe, "Oxygen Reduction Activities of Nanostructured Thin Film Alloy Electrocatalysts", Fuel Cell Seminar, Oct. 13–17, 2008, Phoenix, Abst. 1365.

6. A.J. Steinbach, K. Alade-Lambo, H. Le, and M.K. Debe: "Investigation of Cation-Induced Losses in PEM Fuel Cells", Fuel Cell Seminar, Oct. 13–17, 2008, Phoenix, Abst. GHT35a-22.

7. A.J. Steinbach: "Influence of Contaminants, MEA Components, and Temperature on PEM Fuel Cell Reversible Performance Stability", Canada – USA PEM Network Research Workshop, February 16 and 17, 2009, NRC Institute for Fuel Cell Innovation, Vancouver, BC, Canada.

8. D.A. Stevens, R.J. Sanderson, A. Garsuch, S. Wang, R.E. Mar and J.R. Dahn: "High Throughput Screening of PEM Fuel Cell Catalysts", Canada – USA PEM Network Research Workshop, February 16 and 17, 2009, NRC Institute for Fuel Cell Innovation, Vancouver, BC, Canada.

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13. A.J. Steinbach, H. Le, K Alade-Lambo, C.V. Hamilton Jr., M.J. Kurkowski and M.K. Debe, "Reversible Performance Stability of Polymer Electrolyte Membrane Fuel Cells," Abstract for 238th Am. Chem. Soc. Meeting, Washington, D.C. August 16, 2009.

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V.E.2 Highly Dispersed Alloy Catalyst for Durability

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Subcontractors:

- Johnson-Matthey Fuel Cells, Sonning Commons, UK
- Texas A&M University, College Station, TX
- Brookhaven National Laboratory, Upton, NY

Project Start Date: May 1, 2007

Project End Date: April 25, 2010

Technical Targets

TABLE 1. DOE 2010 Technical Targets for Electrocatalysts and the Current Status of this Project

Characteristic	Units	Project Status as of 06/01/2009	DOE 2010 Target
PGM Total Content	g/kW	0.84	0.3
PGM Total Loading	mg/cm ²	0.64 [†]	0.3
Cost	\$/kW at 47.67/g	~38 [†]	5
Mass Activity	A/mg _{PGM} at 900 mV 9iR-Free)	0.28	0.44
Specific Activity	μA/cm ² at 900 mV 9iR-Free	550	720
Cyclic Durability At T ≤ 80°C At T ≥ 80°C	h h	TBD TBD	5,000 2,000
ECA Loss	%, percent	30*	<40

[†] Anode/Cathode loading – 0.4/0.24 mg_{PGM}/cm².

[†] Based on 5 year average PGM price \$ 47.67/g (Pt = \$1166.22/Troy Oz; Ir = \$316.58/troy oz); costs not projected to high volume production.

* Durability data measured after 30,000 cycles under UTC Power defined accelerated test protocol.

ECA - electrochemical surface area

iR - internal resistance

TBD - to be determined

Objectives

- Develop structurally and compositionally advanced supported alloy catalyst system with loading ≤0.3 mg platinum group metal (PGM)/cm².
- Optimize catalyst performance and decay parameters through quantitative models.
- Demonstrate 5,000 cyclic hours below 80°C with less than 40% loss of electrochemical surface area and catalyst mass activity.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section (section 3.4.4) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- Durability
- Cost
- Performance

Accomplishments

- 30% Pt₄IrCo₃ and 30% Pt₂IrCr were down-selected as the dispersed alloy catalyst systems to be scaled-up for single cell demonstration. Mass activities of ~0.3 A/mg_{PGM} were reproduced in both rotating disk electrode (RDE) and subscale membrane electrode assembly (MEA) testing (3x the activity of standard pure Pt catalyst).
- Dissolution trends of metal atoms other than Pt in Pt-based alloys were evaluated.
- Electronic structure and segregation properties of Pt₃Cr, Pt₂IrCr, and Pt₂IrCo alloys were investigated using quantitative models to determine the most stable surface distributions.
- Surface segregation trends and stability of the surface atoms against dissolution for various shell compositions were evaluated as a function of the shell thickness for Pt monolayer (ML) catalysts on Pd₃Co and Ir cores.

- Catalyst mass activities that surpass the DOE 2010 target for dispersed catalysts ($\geq 0.7 \text{ A/mg}_{\text{PGM}}$) were demonstrated in RDE testing.
- A Pt ML on Pd₃Co/C core-shell catalyst was scaled up from 300 mg to a 5 g batch.
- MEA catalyst layer optimization is in progress.

Introduction

It is well known that, in order for the proton exchange membrane fuel cell technology to become commercially viable, the production cost of the components in a fuel cell must be reduced and, more importantly, the durability of the MEA must be improved. This project focuses on two distinct approaches to the DOE 2010 durability and performance targets. The first approach is the development of a conventional but high performance highly dispersed Pt alloy catalyst on a carbon support. The second system utilizes a novel “Pt ML core-shell” approach capable of achieving very high Pt mass activities [1-3]. Under this latter concept, the main objective is to improve the durability of the cathode catalyst by further optimizing the core material selection, shell thickness of the ML and the particle size of the cores and develop scalable fabrication methods.

Approach

To achieve the objectives on this project, UTC Power (UTCP) has teamed with Brookhaven National Laboratory (BNL), Texas A&M University (TAMU) and Johnson Matthey Fuel Cells (JMFC). Figure 1 shows a schematic of the research focus and the role of all partners. BNL's role comes with over 40 years of experience of Dr. Adzic in the field of fundamental electrocatalysis and spectroscopy. Their role on the project focuses on the development of Pt ML “core-shell” system on various cores including ideal surfaces such as single crystals. In addition, BNL leads our efforts to understand the effect of electronic properties, crystal structure and particle size on activity and durability of this class of electrocatalysts. This is achieved by using advanced spectroscopic techniques such as extended X-ray absorption fine structure (EXAFS) and high angle annular dark field scanning transmission electron microscopy (HAADF-STEM) combined with electron energy loss spectroscopy (EELS). Dr. Balbuena's group at TAMU focuses on development of computational atomistic models to study parameters that influence the activity and durability of core shell and dispersed catalyst systems. The overall scope of JMFC activities in the project encompasses development of (i) dispersed Pt alloy catalysts, (ii) novel synthesis methodologies to scale-up Pt ML core-shell catalysts and (iii) MEA optimization and fabrication.

FIGURE 1. Schematic representation of the UTC Power catalyst project approach and partners. (The arrows represent the relationship between the different tasks and partners.)

Apart from overall project management, UTCP primarily focuses on the development of advanced dispersed Pt-based binary and ternary alloy catalysts. UTCP activities also include modeling support for MEA optimization, fuel cell testing on single-cell level and fabrication and test of a 20-cell short stack for verification.

Results

Molecular Modeling

The main topic that was studied this year was calculation of adsorption energies of atomic oxygen on segregated Pt-skin and non-segregated Pt_3M and Pt_2IrM ($\text{M} = \text{Cr, Fe, Co, and Ni}$) alloy surfaces. The results indicate that in non-segregated Pt_3M alloy surfaces, the adsorption energies of 0.25 ML atomic oxygen follows the trend $\text{Pt} < \text{Pt}_3\text{Ni} < \text{Pt}_3\text{Co} < \text{Pt}_3\text{Fe}$ which is exactly opposite of the trend observed in segregated Pt_3M surfaces. To investigate the origin of the differences between the two types of surfaces, d-band center and d-band filling were calculated along with their main geometric parameters. Table 2 illustrates that the shift of the d-band center for Pt_3M and Pt-skin is very similar, and so is filling of the d-band center. This indicates that electronically, the Pt atoms on skin surfaces differ little from those on the non-segregated alloy surface. It was found that in non-segregated surfaces, electronic effects dominate because the 3-d metals are oxophilic. In contrast, the Pt segregated surfaces are affected by both electronic and geometric effects. In addition, the electronic structure of segregated and non-segregated Pt_3M and PtIrM alloys ($\text{M} = \text{Cr, Fe, Co, and Ni}$) were also correlated to adsorption strength and surface stability against dissolution. Examination of the segregation trends of the Pt_2IrCr alloy reveals that the ordered alloy surface is electrochemically more stable than Pt-skin surfaces against Pt dissolution. The

most favorable Pt skin surface has a composition of PtIrCr_2 in the subsurface. However, the d-band center of the non-segregated surface was found to be -2.3 eV, almost the same as that of the segregated Pt-skin surface (-2.31 eV), denoting similarity of these two electronic configurations.

In the core-shell catalyst concept, the stability and segregation trends of Pt ML on various core materials such as Pd-containing metal cores, IrCo alloyed cores, and different compositions of Ir_xCo_y cores were investigated as a function of several parameters including (a) composition of the Pd in the second layer, (b) the adsorption site for atomic oxygen and (c) the Pt-shell thickness. It is observed that the 1-layer shells offer slightly enhanced resistance for the Pt atoms to dissolve from the surface relative to 2-layer shells, as revealed by the positive potential shift relative to those in a pure Pt (111) surface both under vacuum and in 0.25 ML oxygen. The relative stability decreases for the 2-layer shell, though Pt atoms are still more stable than in pure Pt (111). Based on the above results it was observed that the Pd core enhances the stability of the atoms in the 1-layer shell and the benefit of the Pd core is reduced when the shell thickness increased.

Dispersed Pt Alloy Catalyst

Many factors such as structure, particle dispersion, particle size, type of carbon support used etc, influence the electro-catalytic activity of Pt and Pt alloy nanoparticles. Previously, within this project it was established that a 30 wt% Pt in Pt_2IrCo exhibited an activity almost two times higher than 20 and 40 weight percent samples [4]. In the past year, a significant amount of effort was focused towards development and optimization of the composition of PtIrM ($\text{M} = \text{Co, Cr, Ni, Fe etc.}$) alloy catalysts to further improve electro-catalytic activity and enable lower PGM loading. This involved synthesis, physical characterization (using inductively coupled plasma, transmission electron microscopy and X-ray diffraction), electrochemical characterization in a liquid electrolyte using RDE and verification in an MEA. These catalysts were also subjected to potential cycling. The potential cycling was interrupted at various intervals during the experiment to measure the electrochemical surface area (ECA) and oxygen reduction reaction activity.

Figures 2a and 2b show the ECA and PGM mass activity vs. potential stability during cycling test, respectively, obtained from RDE testing for 30% Pt_4IrCo_3 (DOE 48), 30% Pt_2IrCr (DOE 52) and 30% Pt_6IrCo_7 (DOE 59-1) ternary alloys compared to a commercial TKK 46.4% Pt catalyst. It should be noted that Pt_6IrCo_7 was synthesized in an effort specifically to reduce the total PGM content in the catalyst nanoparticles. The change in ECA with number of potential cycles (Figure 2a) shows that the 30% Pt_4IrCo_3

TABLE 2. Calculated Geometric and Electronic Properties of Pt (111) and Pt_3M (111) Surfaces^a

	interlayer distance (Å)		$\epsilon_d - \epsilon_f$ (eV)	f (%)
	d_{12}	d_{23}		
Pt (111)	2.323	2.283	- 2.40	90.1
Pt_3Fe (111)	2.231	2.263	- 3.11	89.8
$\text{Pt}_3\text{Fe} - \text{Pt skin}$	2.303	2.235	- 3.06	89.3
Pt_3Co (111)	2.221	2.257	- 3.02	89.5
$\text{Pt}_3\text{Co} - \text{Pt skin}$	2.241	2.169	- 2.98	89.3
Pt_3Ni (111)	2.236	2.277	- 2.51	89.6
$\text{Pt}_3\text{Ni} - \text{Pt skin}$	2.238	2.219	- 2.46	89.3

^a d_{12} and d_{23} refer to the distance between the first and second layers and between the second and the third layers, respectively; $\epsilon_d - \epsilon_f$ refers to the d-band center of the surface Pt atoms referenced to the Fermi level; and f is the filling of the d-band of the surface Pt atoms.

FIGURE 2. (a) ECA decay and (b) PGM mass activity decay, as a function of number of potential cycles on various PtIrM ($M = \text{Co}$ and Cr) ternary alloy catalysts obtained from RDE testing in 0.1 M HClO_4 at room temperature between 0.4 (10 sec) and 0.95 (10 sec) V vs RDE.

and 30% Pt_2IrCr ternary alloy compositions are more resistant to loss of electrochemical area compared to the commercial Pt/C. Preliminary results on the 30% Pt_6IrCo_7 alloy catalyst shows a high initial mass activity ($\sim 0.72 \text{ A}/\text{mg}$ of PGM) and ECA ($\sim 91 \text{ m}^2/\text{g}_{\text{Pt}}$). This exceeded previously reported mass activities for state-of-the-art cathode catalysts by approximately 3.5x. The durability of this electrocatalyst under accelerated potential cycling test was $0.3 \text{ A}/\text{mg}_{\text{PGM}}$ after 20,000 cycles. This is approaching the DOE 2010 initial mass activity targets for catalysts.

Figure 3 shows the internal resistance (iR) corrected fuel cell performance curves in H_2/O_2 for the 30% $\text{Pt}_{4.5}\text{Co}_{1.53}$ (DOE 48) and 30% Pt_2IrCr (DOE 52) compared to a standard Gore 57 Pt/C (G57) before and after 30,000 potential cycles. At the beginning of life, the Pt/C shows higher performance compared to the PtIrM ternary alloy catalysts. It should be noted that initial Pt loading in commercial MEA is about two times that of the alloy MEAs used in this project. After 30,000 cycles, the end of life performance (EOL) for the Gore

FIGURE 3. iR corrected fuel cell polarization curves in O_2/H_2 at 80°C ; 100% relative humidity; 150 kPa, for the PtIrM ternary alloys compared to a state-of-art Pt/C MEA before and after 10s – 10s square wave potential subjected between $0.4 - 0.95 \text{ V}$ for 30,000 cycles.

57 Pt/C catalyst is lower than the alloy catalysts in spite of unfavorable loading in alloy MEA. This trend closely follows the results obtained from potential cycling in RDE as shown in Figures 2a and 2b. The benefit of the Ir containing ternary alloy catalysts are evident from the mass activity and ECA under potential cycling shown in Figures 4a and 4b, respectively. The initial mass activity obtained for the 30% Pt_2IrCr (DOE 52) alloy catalyst is $\sim 0.39 \text{ A}/\text{mg}_{\text{Pt}}$ ($0.28 \text{ A}/\text{mg}_{\text{PGM}}$) and EOL activity is $0.22 \text{ A}/\text{mg}_{\text{Pt}}$ ($0.16 \text{ A}/\text{mg}_{\text{PGM}}$). After 30,000 cycles, the mass activity of Gore standard Pt/C is less than $0.1 \text{ A}/\text{mg}_{\text{Pt}}$, a loss of more than 50% whereas the PtIrM ternary alloy catalysts show much lower loss in mass activity ($\sim 30\%$).

Core-Shell Pt Catalysts

The primary focus of core-shell development was (a) to synthesize Pt ML catalysts on Pd_3Co and Ir cores using scalable chemistries without compromising the intrinsic activity of the catalyst as demonstrated by BNL and (b) to characterize the structure of the core-shell catalysts. For this purpose, a large batch (30 g) of Pd_3Co and Ir cores were synthesized at JMFC. Subsequently, a large 5 g batch Pt ML core-shell catalyst was synthesized successfully by JMFC via a chemical method. A 300 mg batch of Pt ML core-shell catalyst was also prepared by BNL using the galvanic displacement of underpotentially deposited (UPD) Cu ML. High mass activities of $>1 \text{ A}/\text{mg Pt}$ are observed for a Pt ML on a carbon supported Pd_3Co nanoparticle on a glassy carbon tip under RDE test conditions. However, correcting for the PGM in the core, the activity normalized to total PGM content is lower than the catalysts prepared via the electrochemical UPD method. Figure 5 shows the mass activity based on PGM loading for three $\text{Pt}_{\text{ML}}/\text{Pd}_3\text{Co}$ core-shell catalysts (i) prepared via Cu UPD on an RDE tip (red) (ii) 300 mg batch prepared using Cu UPD

FIGURE 4. (a) PGM mass activity decay and (b) ECA decay, as a function of number of potential cycles on two PtIrM (M = Co and Cr) ternary alloy catalysts obtained in MEA testing.

FIGURE 5. PGM mass activity vs. RHE for a commercial Pt/C catalysts and a Pt ML on Pd₃Co/C catalysts synthesized via different methods obtained from RDE testing in 0.1 M HClO₄ at 1,600 rpm, and 10 mV/s. The same batch of Pd₃Co/C was used for all Pt ML core-shell catalysts.

(dark blue) and (iii) large scale (5 g) batch prepared via chemical methods (light blue) compared to a commercial TKK 50 wt% Pt/C (black). The Pt_{ML}/Pd₃Co/C prepared via Cu UPD intermediate show mass activities ~1.5 times higher than the standard Pt/C. However, the large-scale Pt core-shell catalyst synthesized via chemical method shows little enhancement on a total PGM basis.

In situ EXAFS studies show that the surface oxidation on Pt_{ML}/Pd₃Co prepared by electroless

FIGURE 6. (a) High resolution STEM images of a PtML/Pd₃Co/C particle synthesized using Cu UPD method and (b) the corresponding cross-sectional compositional line profiles of HAADF-STEM (information of particle size) and Pd M-edge EELS signal (information of Pd distribution along the line) from image (a). The core-shell structure as well as the shell thickness can be directly derived from the difference between HAADF signal and EELS Pd signal.

method is very similar to that of Pt/C. A STEM study indicates that the as-prepared Pt_{ML}/Pd₃Co sample has a broad size distribution, from 3-10 nm. HAADF-STEM profile combined with Pd EELS signal for individual nanoparticles within the catalyst structure provides compelling evidence for the presence of Pt shells around the Pd containing cores as shown in Figure 6 with thickness varying from 0.4-1 nm. Figure 6 shows a representative STEM image obtained for a ~7 nm Pt_{ML}/Pd₃Co/C nanoparticle synthesized using Cu UPD methods and the corresponding HAADF-STEM-EELS profile showing a 0.5-0.6 nm thick Pt shell on a Pd containing core of ~5.5 nm. Similar structural properties are observed for Pt coatings applied to the same Pd₃Co core using the scalable synthesis route.

However, after 6,500 potential cycles between 0.7–1.1 V, these samples show a small particle growth and a similar size distribution compared to the as-prepared catalyst. The particle size change does not account for the total electrochemical surface area loss of the catalysts during cycling. This was found to be consistent with STEM observations which indicate a lower particle density and an uneven shell thickness for the post-cycling test in comparison to the as-prepared sample. Root cause analysis to understand discrepancies observed in core-shell materials synthesized using electrochemical and electroless routes is in progress.

Conclusions and Future Directions

Mass activities of almost 0.3 A/mg_{PGM} in both RDE and subscale MEA testing have been reproduced and verified for a 30% Pt₄IrCo₃ and 30% Pt₂IrCr that have been down-selected as the dispersed alloy catalyst systems to be scaled-up for fuel cell demonstration. A 30% Pt₆IrCo₇ alloy shows a high initial mass activity (~0.72 A/mg_{PGM} RDE) and superior durability capable of meeting the 2010 DOE targets. Pt ML catalyst prepared using scalable chemistries and characterized by a range of techniques show strong evidence for a core-shell structure. A key challenge for the core-shell catalysts is their poor durability towards potential cycling due to non-uniform Pt layer on the core structures. Development of various scalable methods specifically geared towards achieving uniform Pt coatings is an ongoing activity in the project.

Future Directions

- Scale-up and optimization of dispersed alloy catalyst systems in MEAs is in progress aiming to approach high mass activity and more importantly, durability towards potential cycling.
- The fundamental benefit of Ir in PtIrM ternary alloys for durability is being investigated based on their structure and electronic properties.
- Experimental verification of the modeling data for core-shell catalysts based on their stability and activity coupled with results from single-crystal work to be conducted by BNL is expected to close the gap between theoretical surfaces and real catalysts.
- In the case of the core-shell catalysts, preventing dissolution of the core material from the bulk phase of nanoparticles is a major challenge that is being addressed. Our modeling effort continues to drive the search for stable non-PGM cores for core-shell catalyst systems.

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V.E.3 Development of Alternative and Durable High Performance Cathode Supports for PEM Fuel Cells

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Project Start Date: January, 2007
Project End Date: December, 2010

Objectives

Develop new classes of alternative support materials that meet the 2010 DOE performance targets by achieving the following specific objectives:

- Understand structural and compositional requirements of tungsten carbide (WC) and conductive metal oxides (CMOs) for improved activity and durability over standard Pt/C.
- Develop commercially viable processes to synthesize carbon-supported WC and CMO.
- Demonstrate durability and performance advantages of alternative cathode supports such as ordered mesoporous carbon (OMC) and grapheme.

Technical Barriers

This project addresses the following technical barriers from Fuel Cells section (3.4) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research for Fuel Cells, Development and Demonstration Plan:

- (A) Durability (of Cathode Catalyst Supports)
- (C) Performance (of Supported Cathode Catalyst)

Technical Targets

This project is directed at conducting durability and activity studies of Pt on various supports, with the objective of meeting the following 2010 DOE targets for electrocatalyst support for transportation:

- <30 mV loss and <40% electrochemically active surface area (ECSA) loss after 200 hours at 1.2 V/95°C at rated power.
- >5,000 hours at 80°C

Membrane electrode assembly (MEA) tests are in progress for lead supports, and have shown 2X improvement in stability over baseline XC72 supports (Table 1). Alternate supports such as carbon nanotubes (CNTs) have shown no degradation after 100 hours, thus providing a synergistic opportunity for metal oxide modification of CNTs. Rotating disk electrode (RDE) tests have also shown significant improvement in durability over baseline.

TABLE 1. Progress towards Meeting Technical Targets for Electrocatalysts for Transportation Applications

Parameter	Units	2010 Stack Target	PNNL 2009 Status
Accelerated test loss, 200 h @ 1.2 V at 95°C	mV at rated power	<30	MEA tests show 2X improvement over baseline
	% ECSA loss	<40	3-electrode RDE tests show improvement over baseline. TBD for MEA
Durability with cycling at 80°C	Hours	5,000	TBD

TBD – to be determined

Accomplishments

- Model system studies demonstrated Pt agglomeration with stable carbon surface at 1.0 V thus separating Pt agglomeration effects from carbon corrosion.
- Density functional theory (DFT) calculations guided selection of materials with better durability and activity.
- Modification of OMC with WC increased activity.
- CNTs showed higher stability and activity than XC72.
- Modification of carbon supports with metal oxides TiO₂ showed improved (2X) stability.

- Graphene-supported catalysts showed improved activity and stability over XC72 supported catalysts in RDE tests.

Introduction

Conventional cathode catalyst supports are susceptible to corrosion during high potential excursions, high temperature and under start-stop conditions [1]. Hence lack of cathode support durability is a major technical barrier with respect to commercialization of fuel cells for transportation [2]. Oxidation of support leads to detachment of Pt from support, while repeated oxidation and reduction of catalyst leads to dissolution and reprecipitation [3]. The dissolution of platinum is accompanied by penetration of Pt into the membrane or gas diffusion layer, while reprecipitation leads to agglomeration of Pt in the catalyst layer. These lead to an overall decrease in ECSA along with non-uniform current density distribution, leading to sintering of Pt catalysts caused by localized heating.

In order to overcome these barriers and meet the 2010 DOE technical targets for durability and performance, we have developed new classes of alternative and durable cathode supports, based on modifying the carbon surface with WCs [4] and CMOs [5] such as indium tin oxide (ITO), TiO_2 and SnO_2 . Alternate supports such as CNT, graphene sheets were also investigated to take advantage of their superior properties [6,7]. The durability and performance have been enhanced due to the following advantages for our cathode supports:

- Formation of a protective barrier between carbon and Pt mitigates carbon corrosion.
- Bonding between Pt and WC or metal oxide substrates enhances the stability of Pt particles.
- More uniform dispersion of Pt, allowing better performance at equivalent loading.
- Potential synergistic effect due to Pt-like catalytic activity of WC.
- Higher activity and durability of CNT and graphene over XC72 provides potential for an order of magnitude improvement with metal oxide modification.
- Carbon-free metal oxides (ITO) successfully identified as candidates for catalyst support.

Approach

New classes of carbon supports modified by WC and CMO have been developed to improve durability and performance of the cathode catalysts. Various synthesis approaches such as wet impregnation of

platinum precursor onto carbon support and ex situ Pt nanoparticles formation were investigated. In order to prevent alloy formation, ethylene glycol method was selected for all future sample preparation mid-way through the year [8]. Durability of various carbon supports such as XC72, carbon multi-walled nanotubes, mesoporous carbon with various degrees of graphitization and graphene were compared. DFT modeling was performed to identify potential supports with better oxygen reduction reaction (ORR) activity and stability than Pt-XC72. Scanning tunneling microscopy (STM) was done on a Pt-HOPG model system before and after ex situ electrochemical measurements in order to determine degradation mechanism of the supported catalyst. These experiments form a benchmark for examination of alternative supports and electrocatalyst formulations. Carbon supports were modified with WC and various conductive metal oxides such as TiO_2 , SnO_2 , ITO. The durability was investigated using an internally developed accelerated test protocol, with voltage stepped from 1.4-0.85 V vs. normal hydrogen electrode. An investigation of the effect of metal oxide modification of various supports such as multi-wall carbon nanotube, graphene and OMC was conducted. MEA tests were performed on various supports with and without metal oxide modification, with the fuel cell held at 1.2 V at 80°C for 100+ hours, and activity at 0.9 V and polarization curves measured every 20 hours.

Results

In Fiscal Year 2009, MEA tests were conducted on metal oxide modified XC72, along with unmodified alternate carbon supports. We developed a technique to combine STM with ex situ electrochemical measurements for nanoscale resolution of Pt/C electrocatalyst degradation. This technique in conjunction with X-ray photoelectron spectroscopy (XPS) measurements, has solidified our understanding of catalyst-support interactions, which can be applied to various formulations. A cost-effective process was developed for synthesis of high surface area ordered mesoporous carbon with various degrees of graphitization to provide enhanced durability and power density. A modified accelerated test protocol was developed to investigate durability of supported catalysts.

DFT modeling showed that Pt-WC (0001) and Pt-VC (111) have better ORR activity and stability than Pt-C. Figure 1 shows the DFT structures of Pt supported on WC(0001) and CWC(0001). Characterization of model Pt-HOPG systems by scanning electron microscopy (SEM), STM and XPS before and after 9-hour cyclic voltammetry (CV) cycling (0-1 V) indicated Pt agglomeration occurred, while the carbon support remained unchanged (Figures 2a,b). In situ Pt 4f XPS data showed that Pt-support binding energy decreased

FIGURE 1. DFT Structures of WC-Supported Pt

after cycling (Figure 2c), evidence of Pt sintering. These experiments allowed separation of Pt agglomeration from carbon support corrosion, and provide a benchmark for evaluation of alternative supports. Future experiments will look at results for excursion to 1.2-1.4 V and Pt supported on WC.

A commercially viable approach developed in FY 2008 was used to synthesize WC supported on OMC. A wet impregnation method was used to disperse $\text{H}_3\text{PW}_{12}\text{O}_{40}$ precursor on mesoporous carbon which was calcined at different temperatures under hydrogen to form carbide and conductive graphite phases. The oxygen reduction activity for Pt/OMC was enhanced by modification of OMC with WC as shown in Figure 3a.

The mesoporosity was retained after forming WC, with the pore size distribution essentially remaining unchanged (Figure 3b).

MEA tests were conducted on metal oxide modified carbon supports. As shown in Figure 4a, SnO_2 , ITO and TiO_2 modified XC72 provided higher durability after 100-h hold at 1.2 V/80°C. While Pt-XC72 retained 60% of performance at 0.8 A/cm², the corresponding numbers for Pt on SnO_2 , ITO and TiO_2 modified XC72 were 65, 80 and 100%, respectively. Comparison of Pt-XC72 with Pt-CNT showed no degradation for the latter after 110 hours at 1.2 V/80°C, while the XC72 supported catalyst lost 20% in performance at 0.8 A/cm² (Figure 4b). Accelerated testing at 1.4 V hold showed that after 2.3 hours, TiO_2 and SnO_2 modified support had degraded the least (30%), and even outperformed CNT supported catalysts (40% degradation), with Pt-XC72 having degraded by 80% (Figure 5). These results show the immense promise for TiO_2 and SnO_2 -modified CNT as durable supported catalysts.

Performance of carbon-free metal oxide support was investigated using ITO (data not shown). The polarization curves showed a maximum current density of 0.15 A/cm², with no degradation after 20 hours. While the poor performance was due to low ITO surface area, these results show that controlling ITO/carbon ratio can potentially lead to high performance and durability.

Carbon loss was determined by measuring carbon dioxide evolution using mass spectrometry, with the amount of degradation linearly related to carbon loss (data not shown).

FIGURE 2. (a) SEM micrographs of Pt-C before and after 9 hrs CV 0-1 V (b) STM after CV cycling (c) In situ Pt 4f XPS data for fresh Pt/HOPG, exposed to H_2SO_4 , after 180 CV cycles 0-1 V.

FIGURE 3. (a) Activity of Pt on OMC with and without WC 0.05 M oxygen-saturated H₂SO₄ -1,600 rpm, 10 mV/s (b) Pore size distribution for OMC and WC supported on OMC.

While MEA tests are ongoing for graphene supported catalysts, RDE tests showed a 25% increase in activity and a 50% improvement in stability after 5,000 CV from 0.6-1.1 V (Figure 6). Pt had agglomerated after cycling for XC72 supported catalyst, while it remained unchanged for graphene supported catalyst.

Conclusions and Future Directions

Significant progress has been made in development of modeling and analytical techniques to study catalyst support interactions and in synthesis of supported catalysts with higher durability than commercial supported catalysts in RDE and MEA tests:

- Capabilities developed in terms of XPS/ in situ electrochemical tests and STM/ex situ electrochemical tests have been used to study model Pt-HOPG and Pt-WC systems to understand Pt-support interactions and degradation mechanisms.

FIGURE 4. (a) MEA activity and stability of 20% Pt on metal oxide modified XC72 after 60 h hold at 1.2 V/80°C (b) MEA stability after 1.2 V/80°C hold for XC72 and CNT.

- Carbide supports (WC and VC) identified by DFT calculations hold promise for MEAs with high durability and activity.
- Synergistic effect of WC on Pt has been leveraged to develop Pt on WC-modified OMC support with higher activity.
- A 2X better electrochemical durability was demonstrated for TiO₂ and SnO₂ modified XC72 over commercial supported catalysts.
- There was no degradation for CNT-supported catalysts during 1.2 V hold. This provides potential for TiO₂ and SnO₂ modified CNT to have an order of magnitude higher durability than commercial supported catalysts.
- Oxide modification of alternate carbon supports such as OMC and graphene showed better activity and durability in RDE tests.
- Carbon-free metal oxide catalysts (ITO) have been shown to be active towards ORR.

FIGURE 5. Durability of MEAs with CNT, XC72 and metal oxide modified XC72 after 1.4 V/80°C hold for 2.25 h (a) polarization curves, (b) % degradation at 0.5 A/cm².

- The future work will involve investigation of VC-modified carbon supports, metal oxide modified alternate carbon supports such as CNT, OMC and graphene, and continued study of model systems at more aggressive potentials (1.2-1.4 V).

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- Y. Shao, R. Kou, J. Wang, V. Viswanathan, J. Kwak, J. Liu, Y. Wang, and Y. Lin, "The influence of the electrochemical stressing (potential step and potential-static holding) on the degradation of polymer electrolyte membrane fuel cell electrocatalysts", *Journal of Power Sources* 185 280 (2008).
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FIGURE 6. RDE (5,000 CV 0.6-1V) test results for Pt-graphene (a) ESA and activity (b) durability % retained (c) transmission electron microscope (TEM) Pt-Etek (d) TEM Pt-graphene.

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V.E.4 Non-Platinum Bimetallic Cathode Electrocatalysts

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Project Start Date: January 1, 2007
Project End Date: December 31, 2010

Objectives

Develop a non-platinum cathode electrocatalyst for polymer electrolyte fuel cells with the following attributes to meet DOE's technical targets for electrocatalyst activity, durability, and cost:

- Promotes the direct four-electron reduction of oxygen with high electrocatalytic activity (0.44 A/mg Pt or 720 $\mu\text{A}/\text{cm}^2$ @ 0.9 V).
- Chemically compatible with the acidic polymer electrolyte.
- Stable at high potentials and to potential cycling (5,000 h @ 80°C, <40% electrochemical area loss).
- Low cost (\$5/kW).

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) Durability
- (B) Cost
- (C) Performance

Technical Targets

This project is addressing the following 2010 DOE technical targets for electrocatalysts:

- Activity: 0.44 A/mg Pt or 720 $\mu\text{A}/\text{cm}^2$ @ 0.9 V.
- Durability: 5,000 h @ 80°C, <40% electrochemical area loss.
- Cost: \$5/kW, 0.3 mg platinum group metal (PGM)/ cm^2 .

Accomplishments

- Synthesized and determined the oxygen reduction reaction (ORR) activity of palladium-cobalt, rhodium-cobalt, and rhodium-iron alloy nanoparticle systems.
- Highest room temperature nanoparticle ORR specific and mass activity achieved:
 - 95 $\mu\text{A}/\text{cm}^2$ (900 mV; room temperature); 2,420 $\mu\text{A}/\text{cm}^2$ (800 mV; room temperature) for Pd:Cu 1:1 by co-impregnation; 20 nm.
 - 0.06 A/mg Pd for Pd:Cu 1:3 by alternative colloidal; 3.3 nm (900 mV; room temperature)
- Scaled up synthesis of Cu_3Pd electrocatalyst and tested electrocatalyst in membrane electrode assembly (MEA).
- Developed capability to calculate the full valence band structure of pure metals and alloys and correlated the calculated structure of Pt, Pd, and Pd-Cu alloys with experimentally-determined structure.
- Using computational studies, identified several Pd alloys favoring noble metal surface segregation.
- Identified several non-Pt systems having d-band centers similar to Pt's (as a first approximation for choice of systems with desirable electronic structures).
- Fabricated model systems of binary and ternary Pd alloys identified as promising in computational effort.

Introduction

A major contributor to the cost of an automotive polymer electrolyte membrane fuel cell system is the platinum-based cathode electrocatalyst. The goal of this project is to reduce the cost of the cathode catalyst by replacing platinum with less expensive alloys, while also meeting or exceeding the catalyst durability and performance targets.

Approach

The project's approach to meeting the cost, durability, and performance targets is to develop base metal-noble metal alloy nanoparticles with a minor noble metal content, to lower cost, and with the noble metal forming a surface skin or stabilizing the primarily base metal particle core against dissolution in the acidic electrolyte. The initial choice of base metal-noble metal combinations was based on published theoretical calculations predicting the tendency of the noble metal component to segregate to the surface of a base metal substrate and on the ability of the base metal to modify the electronic properties of the noble metal, as reflected by a shift of the weighted average energy of occupied d-band states (i.e., the "d-band center") toward that of Pt [1-4]. The durability of the candidate noble metals (Pd, Rh, and Ir), which tend to be less stable in acidic environments than platinum, is being addressed by shifting the valence band energy of the noble metals, thus decreasing the oxophilicity of the noble metal and imparting stability against dissolution [5-7].

The project's approach includes: (1) computational and model system (pure metals and bulk alloys) studies to guide the choice of systems and noble metal to base metal ratio, (2) nanoparticle fabrication and characterization (ORR activity, particle size, composition, and electronic structure), (3) MEA fabrication and testing, and (4) post-test characterization. Carbon-supported bimetallic nanoparticles are being fabricated by co-impregnation, colloidal, and strong electrostatic adsorption techniques. The co-impregnation technique is used for screening of the catalyst compositions, resulting in relatively large and poly-disperse nanoparticles. The colloidal and strong-electrostatic adsorption techniques are used to form small, mono-disperse particles of the most promising catalyst compositions identified in the co-impregnation screening studies. Spectroscopic techniques are used to determine that the desired nanoparticle bulk and surface composition have been obtained. The oxygen reduction activities of the nanoparticles are being screened using the thin-film rotating ring-disk technique (TF-RDE) [8,9] and the nanoparticle stabilities are screened using potentiostatic and potential cycling measurements in non-adsorbing perchloric acid electrolyte, mimicking the fuel cell ionomer (perfluorosulfonic acid). Materials showing promising ORR reduction activity and stability are incorporated into MEAs and their short and long-term performance determined under accelerated test conditions.

Results

This year we synthesized high-surface-area carbon-supported nanoparticles in the palladium-copper, palladium-cobalt, rhodium-cobalt, and rhodium-iron

systems and determined the effect of noble to base metal ratio and post-deposition heat treatment temperature and atmosphere on ORR activity. The highest ORR activity observed for the rhodium-iron system was 37 mA/mg Rh and 53 $\mu\text{A}/\text{cm}^2$ with a rhodium to iron atomic ratio of 1:1, heat treated at 500°C in 100% hydrogen (@ 0.8 V, room temperature, TF-RDE results). The highest ORR activity for the rhodium-cobalt system was 275 mA/mg Rh and 290 $\mu\text{A}/\text{cm}^2$ (@ 0.8 V, room temp., TF-RDE results) for a catalyst with a rhodium to cobalt atomic ratio of 1:9, heat treated in 4% hydrogen at 300°C and 700°C, respectively. These results show that both iron and cobalt increase the ORR activity of rhodium, but the absolute ORR area-specific and mass activities are far below those of platinum.

This year we also determined the area specific activities for the most promising palladium-copper nanoparticle catalysts, using the hydrogen adsorption/desorption region of the baseline voltammograms to determine the electrochemically-active surface area [9]. As shown in Figure 1, the palladium-copper catalyst with a nominal palladium to copper atomic ratio of 1:3, prepared by the co-impregnation method, heat treated at 600°C, and acid-treated in perchloric acid, showed an area-specific ORR activity comparable to that of commercial platinum (@0.8 V, room temperature, TF-RDE results). Detailed morphological, compositional, and structural characterization of this catalyst by a variety of techniques (electron microscopy, energy-dispersive X-ray emission spectroscopy, X-ray diffraction, and X-ray absorption spectroscopy) showed this catalyst to be comprised of 21.5 ± 7 nm particles with palladium-copper alloy cores (49:51 Pd to Cu atomic ratio), surrounded by a palladium-rich shell. The large particle size of this catalyst relative to that of the commercial Pt catalyst (2.3 nm) means a larger fraction of the noble metal resides in the interior of the particle and does not

FIGURE 1. Room temperature area-specific oxygen reduction reaction activity for Pd-Cu nano-particle catalysts compared to commercial Pt/C (BASF/E-Tek).

participate in the ORR reaction, thus decreasing the catalyst's mass activity. In order to achieve higher mass activities, we attempted to make smaller particles of this same composition and structure, using the colloidal technique to form a 1:1 Pd:Cu core and depositing a palladium shell on this core. The colloidal technique resulted in reduced metal particle sizes of 7-10 nm, but also reduced mass and area-specific ORR activities (Figure 1). We are currently exploring if the reduced area-specific activity results from a particle size effect, as is seen for Pt catalysts [9], or from a different atomic structure. All attempts at deposition of a shell of Pd on both the 1:1 and 1:3 PdCu cores lowered both the mass and area-specific ORR activities of these catalysts.

The stability of the colloidal palladium-copper nanoparticle catalyst with 1:1 and 1:3 Pd:Cu atomic ratios was tested by determining their ORR activity, using TF-RDE, before and after soaking in 0.6 M perchloric acid for three days. As shown in Figure 2, the ORR activity of the 1:1 catalyst was unchanged by treatment for three days in 0.6 M perchloric acid, whereas the 1:3 catalyst showed a dramatic loss of ORR activity. This is attributed to the ability of the 1:1 catalyst to form a stable Pd-rich protective surface, whereas the high copper content of the 1:3 catalyst results in destruction of the structure when leaching copper (as verified by X-ray diffraction analysis). The 1:3 catalyst was also found to be unstable in the fuel cell environment. Testing of the 1:1 catalyst in a membrane-electrode assembly is underway.

In the model system characterization task, the University of Nevada, Las Vegas, has determined the valence band structure of a number of base and noble metal foils using Al $K\alpha$ X-ray photoelectron spectroscopy. These spectra, shown in Figure 3, illustrate that all of the metals have distinct valence

FIGURE 2. Rotating disk electrode results in oxygen-saturated room temperature perchloric acid for Pd:Cu 1:1 and Pd:Cu 1:3 (atomic ratios) synthesized by the colloidal technique before and after acid treatment.

band structures. The vertical bars in Figure 3 indicate the calculated “d-band center” of the respective metals, which has been considered to influence the bonding of oxygenated species to metals and their resulting ORR activity [1-4]. From these data, it can be seen that copper and platinum have similar “d-band center” positions, despite the fact that the actual d-band structures are very different. Likewise, these two metals differ immensely in their bond strength with oxygen and also in their ORR activity [10]. This finding indicates the need for an overall evaluation of the valence band structure rather than using the simplified reduction to the “d-band center” as a figure of merit.

In the computational aspect of the project, the California Institute of Technology is using first principles theory and computation to determine the valence band structure, preferred atomic structures and adsorption sites, ORR reaction pathways and barriers on various metals and metal alloy systems. They calculated the surface segregation energies and “d-band centers” for Pt, Pd, and Rh alloyed with metals in the atomic number range between Sc and Zn (26 systems), Y and Cd (28 systems), and Ta and Hg (21 systems). This survey showed that palladium alloys with molybdenum,

FIGURE 3. Density of states in the valence band for select metal foils and calculated d-band centers.

rhodium, tantalum, or tungsten show favorable segregation of palladium to the surface of the alloy and “d-band centers” approximating that of platinum. However, as mentioned above, the entire valence band structure, its influence on the bond strength with oxygen and oxygenated species, and the complete energetics of the ORR must be determined for these and other alloys. Toward this end, the complete valence band structure for Pt, Pd, Cu, and CuPd, and Cu₃Pd have been determined. As an example, the calculated contributions of the individual wave functions to the valence band structure of copper are shown in Figure 4. This type of calculation and its verification, by comparison with experimentally-determined valence band structures, are the first steps toward analysis of the individual contributions to valence band structures and involvement of these states in the oxygen reduction reaction. This in turn will result in the ability to better predict which non-platinum systems should show ORR activities comparable or higher than the platinum-based catalysts.

FIGURE 4. Calculated individual wave functions, calculated total valence band density of states (summation of individual wave functions), and experimentally-determined valence band density of states for copper.

Conclusions and Future Directions

Conclusions

- Copper modifies the valence band structure and ORR activity of palladium. The extent of the modification of the ORR activity is correlated with the extent of downshift of the valence band density of states.
- Palladium-copper alloy nanoparticles (21 nm), made by the co-impregnation technique, have comparable area-specific ORR activity at 0.8 V to that of platinum.
- Smaller palladium-copper alloy nanoparticles (7-10 nm) made by the colloidal technique have lower area-specific ORR activity.
- d-band center alone does not adequately reflect the valence band structure (density of states as a function of energy) and bond strength of oxygen with metals; the entire spectral distribution must be analyzed.
- Palladium alloyed with molybdenum, rhodium, tantalum, or tungsten shows favorable segregation of palladium to the surface of the alloy and “d-band centers” approximating that of platinum (as a first approximation - entire valence band density of states must be determined).

Future Directions

Computational Analyses

- Based on density functional theory calculations, determine complete energetics for the ORR on Pd-Mo, Pd-Re, Pd-Ta, and Pd-W alloys.
- Continue to determine alloy electronic structures using density of states analysis.
- Investigate solvation effect for the ORR on Pd-based alloys.
- Continue developing reactive force field large-scale molecular dynamic calculations reactive force field for the ORR on relevant alloys.

Model Systems

- Characterize ingots of Pd-Mo, Pd-Re, Pd-Ta, and Pd-W binaries and Pd-Cu-Mo, Pd-Cu-W, Pd-Cu-Re, Pd-Cu-Ta, and Pd-Cu-Ni ternaries with varying Pd to base metal ratios:
 - Determine ORR activity, electronic structure, and surface composition as a function of annealing temperature.

Nanoparticle Fabrication, Activity, and Stability Characterization

- Test of Pd:Cu 1:1 nanoparticle catalyst activity and stability in MEA.
- Synthesis of alloy and core/shell Pd-Cu, Pd-Mo, and Pd-W catalysts using strong-electrostatic adsorption technique.
- Fabricate Pd-Cu-M ternaries and Pd-M binaries using colloidal techniques.

Special Recognitions & Awards/Patents Issued

1. Deborah J. Myers, Xiaoping Wang, Nancy N. Kariuki, “Non-Platinum Bimetallic Polymer Electrolyte Fuel Cell Catalysts”, patent pending.

FY 2009 Publications/Presentations

1. “Bimetallic Palladium-Base Metal Nanoparticle Oxygen Reduction Electrocatalysts”, X. Wang, N.N. Kariuki, S. Niyogi, M. Smith, D.J. Myers, T. Hofmann, Y. Zhang, M. Bär, and C. Heske, Proceedings of the Electrochemical Society (ECS), 2008 Fall Meeting, Honolulu, HI, ECS Transactions 16, 109-119 (2008).
2. “Bimetallic Palladium-Base Metal Nanoparticle Oxygen Reduction Electrocatalysts”, X. Wang, N.N. Kariuki, S. Niyogi, M. Smith, D.J. Myers, T. Hofmann, Y. Zhang, M. Bär, and C. Heske, 214th ECS Meeting, October 12–17, Honolulu, Hawaii, 2008.
3. “First-Principles-based Modeling of Non-Platinum Catalysts for Oxygen Reduction Reaction”, Y. Sha, T. Yu, B.V. Merinov, A. van Duin, and W.A. Goddard III, 214th ECS Meeting, October 12–17, Honolulu, Hawaii, 2008.
4. “First-Principles-based Modeling of Improved Pt Alloy Catalysts”, T. Yu, Y. Sha, B.V. Merinov, A. van Duin, W.A. Goddard III, and P. Shirvanian, 214th ECS Meeting, October 12–17, Honolulu, Hawaii, 2008.
5. “A Rational Method to Prepare Supported Metal Catalysts”, J.R. Regalbuto, Spring AIChE Meeting, Salt Lake City, March, 2009 (invited).

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V.E.5 Advanced Cathode Catalysts

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Project Start Date: March 2007

Project End Date: 2011

- Determine ORR mechanism on newly developed catalysts via extensive physicochemical characterization and electrochemical and fuel cell testing.
- Optimize electrodes with new catalysts and structures for maximum performance.
- Evaluate catalyst stability; minimize performance loss over time.
- Assure path forward for the fabrication and scale up of viable catalysts.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section (3.4.4) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) Durability (of catalysts and electrode layers)
- (B) Cost (of catalysts and membrane electrode assemblies [MEAs])
- (C) Performance (of electrodes, including (i) ORR overpotential and (ii) O₂ mass-transport rates)

Technical Targets

Non-platinum cathode catalysis research in this project focuses on DOE's 2010 technical targets specified in Table 3.4.12 (Electrocatalysts for Transportation Applications) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan. The 2010 targets relevant to this research project together with the current status (where applicable) are:

Characteristics	Units	2010 Stack Target (Anode + Cathode)	2009 Status (Cathode)
PGM total loading (50 cm ² fuel cell)	mg _{PGM} /cm ² electrode area	0.3	0.28 ¹
Mass activity	A/mg _{PGM} @ 900 mV _{IR-free}	0.44	0.34 ² 1.2 ³
Non-Pt catalyst activity per volume of supported catalyst	A/cm ³ @ 800 mV _{IR-free}	> 130	54 ⁴

¹ Pt_{ML}/Pd/C catalyst from scaled-up synthesis by Cabot Fuel Cells, tested in 50-cm² single fuel cell at 80°C; cathode - 0.28 mg_{PGM} cm⁻² (0.06 mg_{Pt} cm⁻² + 0.22 mg_{Pd} cm⁻²); anode - 0.05 mg_{Pt} cm⁻² Pt/C; MEA not optimized

² Mass activity per mg_{PGM} in Pt_{ML}/Pd_{ML}/PdIr/C catalyst in RDE testing at 0.90 V

³ Mass activity per mg_{Pt} in Pt_{ML}/Pd_{ML}/PdIr/C catalyst in RDE testing at 0.90 V

⁴ CM-Fe-C catalyst tested in 5-cm² single fuel cell at 80°C; cathode - 4.0 mg cm⁻²;

anode - 0.25 mg_{Pt} cm⁻² Pt/C; MEA not optimized

PGM - precious group metal

Objectives

The main objective of this project is to:

- Develop an oxygen reduction reaction (ORR) catalyst alternative to pure Pt, capable of fulfilling cost, performance and durability requirements established by DOE for the polymer electrolyte fuel cell (PEFC) cathode.

Individual objectives of this research are as follows:

- Design, synthesize and characterize new catalyst supports and electrode structures for new-generation ORR catalysts.

Accomplishments

- Achieved substantial improvement in mass activity of core-shell catalysts, up to 1.2 A/mg_{Pt} at 0.90 V (in excess of 0.3 A/mg_{PGM}), through the introduction of a Pd interlayer between the nanoparticle core and outer Pt layer.
- Demonstrated much improved stability of nanoparticles in rotating disk electrode (RDE) cycling by (i) addition of Pd interlayer ($\Delta E_{1/2}$ after 30,000 potential cycles reduced from 39 mV with Pt/C to 19 mV with Pt_{ML}/Pd_{ML}/Pd₃Ir/C catalyst), (ii) new synthesis of Pt/Pd₃Fe/C catalyst ($\Delta E_{1/2}$ < 5 mV after 28,000 potential cycles), and (iii) deposition of Au clusters on Pt surface ($\Delta E_{1/2}$ limited to 16 mV after 50,000 potential cycles).
- Completed successful scale up of synthesis of PtIr_{ML}/Pd/C, Pt_{ML}/Pd/C, and Pt_{2ML}/Pd/C using three different methods and without a loss in ORR activity.
- Showed major improvement in ORR activity of non-precious metal catalysts (polyaniline [PANI]- and cyanamide [CM]-derived) in RDE and fuel cell testing; open-circuit voltage (OCV) up to 1.0 V, volumetric activity in excess of 50 A/cm³.
- Demonstrated a non-precious metal catalyst (PANI-Fe₃Co-C) that combines high activity (OCV > 0.90 V, $i_{0.80\text{ V}} = 27\text{ A/cm}^3$) with good stability (ca. 700 hours in H₂-air cell) and negligible peroxide generation (H₂O₂ < 0.5%).
- Determined changes in the chemical state of transition metals during pyrolysis by in situ X-ray absorption spectroscopy (XAS) methods; demonstrated enhanced surface-specificity of X-ray absorption near-edge spectroscopy (XANES) by operating at Co and Fe L-edge (important step in determination of the ORR active-site in non-precious metal catalysts).
- Initiated mechanistic analysis of ORR kinetics at non-precious metal catalysts and modeling of thick non-precious metal catalyst layers.
- Developed, catalyzed with Pt, and incorporated into MEAs cathode structures based on multi-walled carbon nanotubes with an unusually long length of ~300 μm , capable of delivering very good per-mass performance of 0.75 A/mg_{Pt} (overall performance in need of improvement).

Introduction

This multitask and multi-partner project focuses on the development of new oxygen reduction catalysts and electrode structures for the PEFC cathode, with either greatly reduced precious-metal content relative to that

presently used by stack developers, or entirely precious-metal-free. The main objective of this effort is to lower the catalyst cost in the fuel cell power system through improvements in ORR performance in terms of both electrocatalysis and oxygen transport to the reaction site.

Approach

The primary research goal of this project is the development of new oxygen reduction catalysts, in two different classes: (i) catalysts with ultra-low platinum content (stable metals or alloys as cores; non-precious-metal core catalysts; mixed metal shells for higher ORR activity) and (ii) precious metal-free catalysts (low- and high-temperature catalysts based on transition metals precursors). Catalyst characterization, both electrochemical (in aqueous electrolyte and in the fuel cell) and ex situ, is a major part of the effort, focusing on such key challenges as ORR active-site identification and catalyst durability.

Development of new catalysts is closely tied to novel electrode structures, tailored to maximize either catalyst utilization in the case of precious-metal-based ORR catalysts (e.g. core-shell Pt-based catalysts) or loading of non-precious metal catalysts with intrinsically lower than platinum volumetric ORR activity. The electrode-structure component of the effort concentrates on two groups of materials: (i) templated nanostructures, such as nanofibers and nanotubes, made of polymers (e.g. polypyrrole), carbon, and non-carbon inorganic materials, and (ii) open-frame catalyst structures obtained using microemulsion/reverse emulsion method and other techniques.

In addition to short-term testing and initial performance assessment, catalysts, supports, electrode structures, and MEAs, developed in this project are subject to long-term performance (durability) testing. Performance degradation mechanisms are being identified and, if possible, addressed. Fabrication and scale up of viable catalysts and supports is also being tackled through collaboration between partners in this project.

Results

Catalysts with Ultra-Low Pt Content – In the past year, we developed several core-shell catalysts in this category using Pd interlayer between non-platinum core and Pt-monolayer shell. Thanks to assuring better match with the lattice constant of Pt, “smoothing” the core surface, and providing oxide-free support for Pt layer, the Pd interlayer presence leads to catalysts with very respectable ORR performance relative to that of similar catalysts without the Pd interlayer or that of a standard Pt/C catalyst (Figure 1). The half-wave potential ($E_{1/2}$) of the most active catalysts in RDE testing (Pt_{ML}/Pd_{ML}/Pd₃Ir/C and Pt_{ML}/Pd_{ML}/PdIr/C) is by 50-60 mV

FIGURE 1. RDE performance of core-shell catalysts with Pd interlayer: (a) ORR polarization plots for five catalysts; (b) ORR activity per Pt mass (left) and total precious metal mass (right); (c) ORR polarization plots for Pt_{ML}/Pd_{ML}/Pd₃Ir/C before and after 30,000 cycles between 0.70 and 0.95 V vs. reference hydrogen electrode, cell temperature = 25°C.

more negative than that of the reference Pt/C catalyst (Figure 1a). This significant $E_{1/2}$ advantage is the reason for mass activity improvement when referred to the Pt mass and total PGM mass in the catalysts with Pd interlayer (Figure 1b). The mass activities at 0.90 V of the best performer in this group (Pt_{ML}/Pd_{ML}/PdIr/C) are 1.2 A/mg_{Pt} and 0.34 A/mg_{PGM} at 0.90 V (RDE testing, room temperature). The latter mass activity number comes within ~80% of the DOE target of 0.44 A/mg_{PGM}. Notably, the catalysts in this group combine high ORR activity with much improved performance durability. As shown in Figure 1c, the $E_{1/2}$ loss for a Pt_{ML}/Pd_{ML}/Pd₃Ir/C catalyst after 30,000 potential cycles between 0.7 and 0.95 V is only 19 mV, much less than a 39 mV loss observed with the Pt/C catalyst.

Better stability of catalysts in this category was also achieved by two other approaches: (i) addition of Au clusters to the surface of Pt nanoparticles and (ii) new synthesis of Pt/Pd₃/Fe/C catalysts. In the first case, the $E_{1/2}$ shift after 30,000 potential cycles is reduced from 43 mV for untreated Pt/C catalyst, 8 nm in average particle size, to 16 mV for the same Pt/C catalyst but modified with Au clusters (approximate stoichiometry of PtAu_{0.12}/C, nominal Au coverage of 0.6 monolayer,

ML). Given the partially non-precious character of the core, even more remarkable durability was achieved with the Pt/Pd₃/Fe/C catalyst (Figure 2). The well-alloyed ~10 nm nanoparticles of that catalyst (cf. transmission scanning microscopy [TEM] in Figure 2a) not only show very high ORR activity (~1.0 A/mg_{Pt}, $E_{1/2}$ 0.865 V) but also virtually no activity loss after 28,000 cycles (Figure 2b).

Scale-up Synthesis of Catalysts with Ultra-low Pt Content – Using two electrochemical techniques (Cu-underpotentially deposited [UPD] displacement and Cu-UPD-mediated layer-by-layer growth), the Brookhaven National Laboratory team scaled up the synthesis of three core-shell catalyst systems to 2-5 gram quantities in a single batch without a loss in the ORR activity of the catalysts. The mass activities of the three catalysts are as follows: PtIr_{ML}/Pd/C – 0.66 A/mg_{Pt} (0.24 A/mg_{PGM}), Pt_{ML}/Pd/C – 0.57 A/mg_{Pt} (0.21 A/mg_{PGM}), Pt_{2ML}/Pd/C – 0.38 A/mg_{Pt} (0.17 A/mg_{PGM}). The catalyst composition was confirmed using inductively coupled plasma and XAS analysis; the core-shell structure of nanoparticles was verified by high angle annular dark field scanning transmission electron microscopy imaging.

FIGURE 2. Pt/Pd₃Fe/C core-shell catalyst: (a) TEM image; (b) ORR polarization plots before and after 28,000 cycles between 0.70 and 0.95 V vs. RHE.

A gram-scale synthesis of the Pt_{ML}/Pd/C catalyst was independently accomplished by Cabot Fuel Cells using a spray-pyrolysis approach. The catalyst delivered very good performance in fuel cell testing (Figure 3), reaching mass-activity of 0.55 A/mg_{Pt} and 0.12 A/mg_{PdGM} at 0.90 V, much better than that of a reference Pt/C catalyst (Figure 3).

Precious Metal-Free Catalysts – The focus of research in this catalyst category was on materials obtained by heat-treating carbon supported precursors, predominantly polypyrrole (PPy), CM, and PANI, in the presence of transition metal salts, mostly salts of Fe and Co. In some cases, two transition metal salts were used at the same time. Several catalysts with very high ORR activity were synthesized, using both PANI and CM as precursors. In particular, PANI-derived catalysts were optimized for maximum ORR activity in RDE testing. These catalysts exhibit gradual improvement

FIGURE 3. Fuel cell testing of a Pt_{ML}/Pd/C catalyst from a scale-up synthesis by Cabot. Anode – 0.05 mg_{Pt}/cm², 1.5× H₂ at 1 A/cm²; cathode – 2.5× air at 1 A/cm²; MEA area – 50 cm²; cell temperature – 80°C; anode/cathode relative humidity – 100%; anode/cathode backpressure – 30 psig; data acquisition – 10 min/point; membrane – Nafion® 212.

in performance as the composition and heat-treatment temperature are optimized (Figure 4a). Rotating ring disc electrode (RRDE) data show that an increase in ORR activity correlates well with enhanced selectivity for the four-electron reduction of O₂, i.e. with reduced hydrogen peroxide yield (Figure 4b). The best RDE performance to date was achieved with PANI-Fe-C and mixed-metal PANI-Fe₃Co-C catalysts, which produce ORR onset potential higher than 0.90 V, half-wave potential of ~0.77 V, and H₂O₂ yield lower than 0.5%.

High ORR activity of several PANI-derived catalysts was confirmed in fuel cell testing, both on neat oxygen and air. PANI-Fe₃Co-C generated the open-cell voltage of 0.91 V and 0.93 V on air and oxygen, respectively (Figure 5). Volumetric activity of the catalyst was measured at 19 A/cm³ on air and 27 A/cm³ on oxygen at 0.80 V. Notably, PANI-Fe₃Co-C and a few other PANI-derived catalysts combine high ORR activity with very promising stability. As shown in Figure 5b, little performance loss is seen with PANI-Fe₃Co-C catalyst during nearly 700 hours of testing in an H₂-air fuel cell at 0.40 V.

The highest ORR activity in an operating fuel cell was measured with a CM-Fe-C catalyst, heat-treated at 1,050°C. While trailing PANI-derived catalysts in durability, the CM-Fe-C catalyst yields OCV of ~1.0 V and volumetric activity of 54 A/cm³ at a fuel cell operating voltage of 0.80 V. RDE testing reveals very high selectivity of the CM-Fe-C catalyst, with peroxide yield remaining below 0.4%, regardless of the operating potential (down to 0.0 V) and independently of the catalyst loading at the disk (40-800 µg/cm² range).

We recently initiated mechanistic analysis of ORR kinetics at non-precious metal catalysts. The approach

FIGURE 4. RDE/RRDE performance of PANI-derived catalysts at 25°C: (a) ORR polarization plots; (b) H₂O₂ generation plots as a function of potential (ring data). Catalyst loading – 0.12 mg cm⁻²; electrolyte – 0.5 M H₂SO₄; scan rate – 5 mV/s; disk rotation rate – 900 rpm; reference electrode – Ag/AgCl (3M NaCl); counter electrode – Au-mesh; cell temperature – 25°C.

assumes participation of a reversible redox couple on the surface of Fe-based catalysts (cyclic voltammetry data) as mediator in the ORR process. Preliminary calculations reproduced experimental ORR Tafel plots for PANI-Fe₃Co-C at various catalyst loadings. The calculations also point to the intrinsic properties of the catalyst as being responsible for the Tafel slope curvature at the most extreme overpotentials.

We also started modeling catalyst layers to minimize mass-transport losses in thick electrodes made of non-precious metal catalysts with relatively low volumetric activity (the result of low turnover frequency and/or low concentration of ORR active sites). The focus of this effort is water evaporation and capillarity as main factors contributing to catalyst flooding and mitigation strategies to prevent water accumulation.

FIGURE 5. Fuel cell performance of a PANI-Fe₃Co-C catalyst: (a) polarization plots; (b) 700-hour life test on air at 0.40 V. Anode – 0.25 mg cm⁻² Pt (E-TEK), 30 psig; cathode – 4.0 mg cm⁻² PANI-Fe₃Co/C; 30 psig air/O₂; membrane – Nafion®1135; cell temperature – 80°C.

In X-ray absorption in situ and ex situ experiments at the Advanced Photon Source and Stanford Linear Accelerator Center, we determined chemical changes in the transition metal state during pyrolysis. We also demonstrated enhanced surface-specificity of XANES by operating at Co and Fe L-edge. The latter experiments may prove crucial in the effort aimed at identifying the ORR active site(s) in non-precious metal catalysts.

Catalyst Structures – One of many challenges facing cathode catalysis research is the development of new electrode structures. In the past year, our effort concentrated on catalysts supported on carbon nanostructures and also carbon-based electrodes with hierarchical porosity. Among other accomplishments, we developed, catalyzed with Pt, and incorporated into MEAs cathode structures based on multi-walled carbon nanotubes (MWNTs) (Figure 6). Once used in the cathode, the unusually long (~300 μm) Pt-catalyzed MWNTs are capable of delivering excellent per-mass ORR performance (0.75 A/mg_{Pt}). However, because of extremely low Pt loading used (12 μg/cm²), the absolute

Figure 6. MWNT-supported Pt catalyst: (a) TEM images; (b) MEA fabrication method.

performance of a MWNT-based cathode is inadequate for meeting power requirements of most fuel cell systems and needs to be improved.

Conclusions and Future Directions

- Core-shell catalysts with greatly reduced Pt loading offer much better ORR performance in aqueous electrolytes and in hydrogen-air fuel cells than standard carbon-supported Pt catalysts; based on measured RDE activity, these catalysts stand a very good chance of meeting 2010 DOE stack performance targets, provided de-alloying and catalyst agglomeration can be avoided (recent durability data are very encouraging in that regard); development of a methodology for increasing the number of high-coordination surface atoms of core-shell nanoparticles to enhance their ORR activity and stability will be the main research task in this part of the project.
- Several non-precious metal catalysts, mostly PANI-derived, exhibit much improved ORR activity, very good selectivity for the four-electron

oxygen reduction and promising fuel cell stability for hundreds of hours; in spite of this significant progress, all non-precious metal catalyst are in need of further activity improvement, by at least of a factor of five; the focus of future research will be on (i) increasing ORR activity, (ii) assuring stability, and (iii) determination of the active ORR site using a wide range of available techniques, X-ray-based in particular.

- Susceptibility of carbon-rich non-precious catalysts to flooding continues to be a major performance issue for non-precious catalysts, especially at high current densities; future research will focus on designing electrode structure amenable to more efficient water management than traditional MEA designs.
- Novel electrode structures based on nanostructures potentially offer considerable performance advantages over dispersed carbons and improved catalyst utilization; future research will concentrate on taking full advantage of the unique morphological and, possibly, electrocatalytic properties of these materials.

Special Recognitions & Awards/Patents Issued

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2. The 7th Spring Meeting of the International Society of Electrochemistry, Szczyrk, Poland, March 22-25, 2009. Title: "New Non-precious Oxygen Reduction Catalysts for Polymer Electrolyte Fuel Cells;" P. Zelenay, G. Wu, H.T. Chung (invited lecture).
3. Canada-USA PEM Network Research Workshop, Vancouver, Canada, February 16-17, 2009. Title: "Progress in the Development of Non-precious Fuel Cell Cathode-Catalysts at Los Alamos National Laboratory;" G. Wu and P. Zelenay (invited lecture).
4. 214th Meeting of The Electrochemical Society, Honolulu, Hawaii, October 12-17, 2008. Title: "A Non-Precious Electrocatalyst for Oxygen Reduction Based on Simple Heat-Treated Precursors;" H. Chung, C. Johnston, F. Garzon, and P. Zelenay.
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- 13.** Nanyang Technological University, Singapore, August 6, 2008. Title: “Synchrotron Photoemission of Metal/Alloy Nanoparticles in Reference to Fuel Cell Electrocatalysis;” A. Wieckowski.
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V.F.1 Platinum Group Metal Recycling Technology Development

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Contract Number: DE-FC36-03GO1314

Consultant:

Ceralink, Troy, NY

Start Date: October 1, 2003

Projected End Date: October 31, 2009

- Cost - \$7/kW (based on \$1,100/troy ounce of platinum)
- Total Pt catalyst loading – 0.20 g /kW

Accomplishments

The following tasks related to development of the process for precious metal recovery from fuel cell MEAs were performed in the past year:

- Identified two competitive material preparation technologies, granulation and cryo-milling/agglomeration, that are compatible with the process of leaching Pt from used MEAs.
- Determined critical elements of leaching chemistry, resulting in 98% Pt yield in a single leach.
- Performed corrosion studies of titanium, a potential reactor material, under modified leach conditions, and demonstrated the potential for a 10-fold increase in corrosion resistance using a copper additive.
- Refined the original process flow diagram and the economic analysis based on the technical improvements made over the last year, including 85% reduction in acid consumption.
- Validated a technology for near-quantitative removal (>99%) of phosphoric acid from polybenzylimidazole (PBI)-based MEAs.

Objectives

Develop a new process for precious metal recovery from polymer electrolyte membrane electrode assemblies (MEAs), while eliminating hydrogen fluoride emission, a disadvantage of the current combustion-based recycling process.

Technical Barriers

This project addresses the following technical barriers from Section 3.4.4 (Technical plan/Barriers) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

(B) High Cost of Catalyst Materials

Technical Targets

The cost of the fuel cell stack will depend on the price of precious metals, which will be impacted both by the amount of precious metals used in the stack and by the development of a cost-effective recycling process. The 2015 targets for precious metal content and cost for transportation applications are as follows:

Introduction

Precious metals are enabling materials in the fuel cell, both for the fuel reformer that generates hydrogen and the fuel cell itself, where the hydrogen is consumed. The precious metals used, Pt, Pd, Rh and Ru, are limited in nature, and recycling is required to ensure that market forces do not make the fuel cell economically unattractive. A study by TIAX has shown that by 2050, recycled Pt will overtake freshly-mined Pt as the dominant source of metal for the fuel cell market [1].

Over the last year, the leaching process proposed in 2008 to recover Pt has been radically improved, resulting in a simpler process that requires a single leach and rinse cycle that is carried out in one vessel.

Approach

Last year, a two-stage leach was proposed to achieve 98% recovery of the Pt contained in MEAs. Over the last year, an effort was made to improve the yield of the process, with an objective of requiring only one leach, with investigations into reagent selection and

usage. Also, work was performed to simplify material handling and safety issues, as well as to investigate the potential for corrosion of a titanium-lined reactor. Process improvements noted in bench scale testing were validated in scaled-up testing.

Results

Cryo-milling had previously been validated as a mechanism to prepare MEAs as a powder that could be sampled in-line, but the resultant hydrophobic product required wetting with an aqueous surfactant to leach Pt successfully. Alternatives to this process were identified over the last year. It was found that the milled MEA powder could be agglomerated using a hot melt process. The resulting coarse powder was hydrophilic and porous enough for efficient leaching. Pt recoveries of >99% were reported in a single leach. However, an alternative was desirable because of the complexity and cost of using liquid nitrogen for MEA pre-embrittlement and mill cooling. Granulation was identified as a viable, room temperature alternative to cryo-milling. In one trial, 5-layer MEAs made with gas diffusion layers (GDLs) of either carbon cloth (gas diffusion electrode, GDE) or carbon paper (catalyst-coated membrane, CCM) were granulated with a Press Side Granulator (Hosokawa Polymer Systems). The fluffy products were leached with efficiency of ~98% in a single step. In a second, scaled-up trial with MEAs made with carbon cloth (GDE), a denser product was achieved. Leaching of this material resulted in Pt recovery in excess of 99%.

The high Pt yield reported above was far better than project results previously reported for a single leach

step. This improvement was achieved, in some degree, by successive changes in the leaching process. First, the amount of surfactant decreased; for the granulated MEA, the surfactant was reduced 5- to 10-fold by using sonication to stimulate material dispersion. Next, the amount of nitric acid used for the leaching was decreased from the amount required for reaction with hydrochloric acid (HCl) to yield aqua regia to ~15% of the stoichiometric amount required to react with HCl. Third, the order of acid addition was studied. Dosing with concentrated HCl and then limiting HNO_3 usage resulted in consistently high Pt yields, whereas lower yields were achieved when HNO_3 was added first. For agglomerated powders, 99% of Pt was recovered and, for granulated MEAs, the results ranged from 97 to 99% for carbon fiber GDEs and 98% for CCMs with carbon paper GDLs, respectively. When azeotropic HCl was used in place of concentrated HCl, Pt yields decreased 3-5% for the agglomerated samples. The conclusion from the various experiments was that high chloride concentration promoted Pt recovery. A result of decreased HNO_3 usage is that >80% of the HCl initially added can be recycled. Since concentrated HCl optimizes Pt recovery, the HCl/water azeotrope generated during HCl distillation will have to be treated using an azeotrope breaker to recycle HCl as the concentrated acid. Figure 1 shows a representation of the overall Pt recycling process with the granulation option.

Trying to reach quantitative Pt recovery is desirable because of the high cost of Pt; a 1% Pt loss was estimated to be equivalent to a revenue loss of about \$3.50/kg of MEA, assuming 1% wt/wt Pt and a cost of \$1,100 per troy ounce of Pt. It was shown that the

FIGURE 1. Revised Process Flow Diagram

Pt yield from the granulated GDE could be increased by 1% if the residue was sonicated in an alkaline rinse, a medium that also neutralizes the residue prior to disposal. Sonication adds almost no cost to the process and more effectively rinses the MEA residue than conventional methods. Similarly, very high Pt recovery is achieved using the agglomeration approach, at a slight increase in processing cost. For example, the combination of cryomilling and agglomeration increases the process cost by an estimated \$0.60/per kg MEA (<20% of the value of the increased Pt yield) compared to the granulation and surfactant wetting process alternative. The cost differential is based on LN_2 cost and higher reagent usage.

Data for the optimized leaching process, including both lab runs with sonification-intensified rinsing and scale-up data, are shown in Table 1. The scale-up of the leaching process, using a stirred titanium Parr reactor, successfully demonstrated near quantitative Pt yield when the experiment was run at 100°C, independent of nitric acid usage (15 or 100% of aqua regia stoichiometry). Minimizing HNO_3 added is highly preferred economically and environmentally, but affects the corrosion resistance of titanium. The impact of temperature, oxidant and corrosion inhibitors on a titanium vessel is shown in Figure 2. Operating at 100°C

TABLE 1. Data for Optimized Leaching Process

A. Representative Leach Data for Granulated/sonicated GDEs

Rinse	mg F	mg rinse	mg R	mg T	% Pt yield
NaOH	49.10	0.37	0.36	49.83	99.28
NaOH	54.63	0.42	0.30	55.35	99.46
Water	51.70	0.25	0.39	52.34	99.25
Water	54.60	0.24	0.40	55.24	99.28

mg F - mg of Pt in filtrate; mg rinse - mg Pt in the sonicated rinse;
mg R - mg Pt in the residue; mg T - total mg Pt

B. Representative Leaching Data from 600-mL Parr Reactor Runs

Sample ID	HNO_3 , % of aqua regia stoichiometry	Temperature	% Pt yield
Milled GDE	100	100	98.6
Agglomerate A	100	100	99.5
Agglomerate B	100	100	99.5
Agglomerate A	100	100	99.5
Agglomerate A	100	100	99.3
Agglomerate A	10	100	99.5
Agglomerate B	100	90	96.5

FIGURE 2. Comparison of Corrosion Rates for Titanium at 100 and 150°C

reduces corrosion by an order of magnitude compared to 150°C, and the loss of passivation of titanium as a result of using less nitric acid in the leach can be offset by addition of copper sulfate.

Whereas Nafion® is used as the membrane for low-temperature fuel cells, high-temperature (180°C) fuel cells, which are relatively immune to CO poisoning, are constructed using phosphoric acid-saturated PBI membranes. Removing the H_3PO_4 prior to acid leaching is desirable; otherwise, phosphorus will enter the precious metal purification process. Water leaching of the PBI membranes is only partially effective; roughly 80% of the acid is removed using water leaching and this is not improved using sonication. An extended sonication study was performed in conjunction with MEC Chemicals. Half inch wide strips of MEAs were treated at room temperature with either water only, a single proprietary reagent, or successive treatments with two proprietary reagents. The impact of treatment time and use of a cold water rinse were also studied. During the study, all virgin MEA samples delaminated, while the strips of aged MEAs stayed laminated. The residual H_3PO_4 in the strips was determined using inductively coupled plasma after an acidic extraction was performed. The achievement of 99% H_3PO_4 removal from both virgin and aged MEAs is remarkable, particularly since the membranes of the aged MEAs were not in direct contact with the extractant. The validity of the test results was checked by milling the extracted samples and checking for residual acid. The re-extraction of the milled samples showed an insignificant amount of acid remaining. The comparison of the different sonication-activated H_3PO_4 extraction processes is shown in Figure 3.

Based on unit operations testing, a revision was made to the pilot plant proposed in 2008. The new estimate is roughly \$1.5MM. The plant is sized to process 1 kg batches of MEAs.

FIGURE 3. Improvement in H_3PO_4 Leaching using Proprietary Extraction Agents

Conclusions and Future Directions

- Using a semi-optimized process, up to 99% Pt recovery from MEAs in a single leach has been demonstrated under lab conditions. Changes in the process conditions contribute to increasing free HCl concentration.

- Alternative technology, including granulation and agglomeration, has been evaluated to improve wetting of the hydrophobic MEA powder prior to leaching. For example, sonication improves MEA dispersion while reducing the amount of surfactant required roughly 10-fold.
- A 600-mL Si-passivated titanium-lined high-pressure reactor is being used to optimize process conditions (temperature, pressure, agitation). >99% Pt recovery has been achieved in a single leach.
- Ultrasonic pre-treatment to remove phosphoric acid from PBI-based MEAs results in almost quantitative removal of the acid.

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V.G.1 Nitrided Metallic Bipolar Plates

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Project Start Date: May 1, 2007

Project End Date: September 30, 2010

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) Durability
- (B) Cost
- (C) Performance

Accomplishments

- Designed and manufactured stamped serpentine 16 cm² active area anode and cathode plates using 0.1 mm stainless steel foil and modified associated fuel cell test stand hardware to permit durability testing under cyclic single-cell fuel cell test conditions.
- Completed single-cell fuel cell evaluation of stamped, untreated 904L, 2205, and Fe-20Cr-4V stainless steel foils, stamped and pre-oxidized/nitrided 2205 and Fe-20Cr-4V stainless steel foils, and machined graphite plates of similar flow field design.
- Stamped and pre-oxidized/nitrided Fe-20Cr-4V stainless steel foil exhibited comparable voltage-current (V-I) performance curves to benchmark graphite plates over 1,000 h of cyclic single-cell fuel cell testing. Post-test analysis of the MEA by X-ray fluorescence indicated levels of metal ion contamination of only $0.1\text{--}0.3 \times 10^{-6}$ g/cm² for both pre-oxidized/nitrided Fe-20Cr-4V and graphite plates. This level of contamination is in the range of the fresh MEA starting levels and indicates excellent resistance to metal ion dissolution by the stamped and pre-oxidized/nitrided Fe-20Cr-4V foil.

Objectives

- Develop and optimize stainless steel alloys amenable to formation of a protective Cr-nitride surface by gas nitridation, at a sufficiently low cost to meet DOE targets and with sufficient ductility to permit manufacture by stamping.
- Demonstrate capability of nitridation to yield high-quality stainless steel bipolar plates from thin stamped alloy foils (no significant stamped foil warping or embrittlement).
- Demonstrate single-cell fuel cell performance of stamped and nitrided alloy foils equivalent to that of machined graphite plates of the same flow-field design (~750-1,000 h, cyclic conditions, to include quantification of metal ion contamination of the membrane electrode assembly [MEA] and contact resistance increase attributable to the bipolar plates).
- Demonstrate potential for adoption in automotive fuel cell stacks.

Introduction

Thin stamped metallic bipolar plates offer the potential for (1) significantly lower cost than currently-used machined graphite bipolar plates, (2) reduced weight/volume, and (3) better performance and amenability to high volume manufacture than developmental polymer/carbon fiber and graphite composite bipolar plates. However, most metals exhibit inadequate corrosion resistance in proton exchange membrane fuel cell (PEMFC) environments. This behavior leads to high electrical resistance due to the formation of surface oxides and/or contamination of the

TABLE 1. Status of Key Technical Targets Relevant for Metallic Bipolar Plates* (Targets obtained from DOE 2007 program plan (where noted) and internal ORNL assessment based on industrial input.)

Material wt%	¹ Polarization (10^{-6} A/cm ²)		ICR (mohm-cm ²), <u>both coupon faces</u> , load of 150 N/cm ²		⁴ Estimated alloy cost \$/lb
	Anode	Cathode	As-Received	¹ Polarized	
Targets	² <1	² <1	≤20	≤20	<7
Untreated Benchmark Stainless Steel Sheet Material					
316L Metal	³ +12	11	300 ⁺	300 ⁺	3-7
446 Metal	-1	1	400	500	3-7
Nitrided Sheet Material					
Ni-(30-50)Cr	-3	<1	15-20	20 to 20-40	> 15
446	-1	1	10	20-30	3-7
Fe-27Cr-6V	-6	1-2	10	20	7-15
Fe-20Cr-4V	-1 to -8 range	3-14 range	10	15-20	5-10
Untreated Stainless Steel Foils					
2205	-8	50	670	not checked	3-7
Fe-20Cr-4V	-20	500	370	not checked	5-10
Nitrided Stainless Steel Foils					
2205	-4	1	20-50	50-100	3-7
Fe-20Cr-4V	-3	6	15-20	40-50	5-10

1. NREL screening protocol. ~7.5 h in 70°C 1M H₂SO₄ + 2 ppm F at 0.84 V vs SHE (cathode, aerated) and 0.14 V vs SHE (anode, H₂-purged). These conditions represent an accelerated, highly aggressive screening evaluation. Internal ORNL project target current densities are $\leq \sim \pm 5 \times 10^{-6}$ A/cm².

2. DOE 2010 targets. The test environment, conditions, and potential are not specified.

3. "+" current under anode conditions suggests metal dissolution which could lead to MEA contamination.

4. Estimated alloy cost by ORNL and GenCell to meet DOE bipolar plate cost target of \$5/kW.

*Corrosion and ICR measurements by Wang and Turner, NREL.

ICR – interfacial contact resistance; SHE – standard hydrogen electrode

MEA by metallic ions, both of which can significantly degrade fuel cell performance. Metal nitrides offer electrical conductivities up to an order of magnitude greater than that of graphite and are highly corrosion resistant. Unfortunately, most conventional coating methods (for metal nitrides) are too expensive for PEMFC stack commercialization or tend to leave pinhole defects, which result in accelerated local corrosion and unacceptable performance.

Approach

The goal of this effort is to scale up and demonstrate the technological and economic viability of thin (≤ 0.1 mm) stamped metallic bipolar plates protected by a thermal (gas) nitrided surface. Proper selection of bipolar plate alloy composition and nitridation conditions can yield a pin-hole free, electrically conductive and corrosion resistant Cr-nitride based protective surface layer. Proof-of principle evaluation of nitrided model Ni-Cr base alloys (see Table 1) indicated that thermally grown Cr-nitride base surfaces exhibit excellent corrosion resistance and maintain low interfacial contact resistance (ICR) in PEMFC environments, and based on single-cell fuel

cell studies, [1-3] have the potential to meet the DOE 5,000 h durability goals for automotive applications. Unfortunately, nickel-base alloys are too expensive for automotive PEMFC bipolar plate applications. Iron-base stainless steel alloys can potentially meet the DOE cost targets. However, they exhibit high permeabilities to nitrogen, which results in internal Cr-nitride precipitation on nitriding instead of the desired continuous, protective Cr-nitride surface layer.

Efforts at ORNL and NREL [2-4] have identified an approach to bypass the high nitrogen permeability of Fe-Cr base stainless steels to permit protective Cr-nitride surface layer formation. It is based on pre-oxidation to form a Cr-rich oxide surface, followed by conversion of the surface Cr-oxide to Cr-nitride on nitriding. Small additions of vanadium to the alloy improve the behavior by modifying the Cr-oxide to make it more amenable to nitriding. Model pre-oxidized and nitrided Fe-27Cr-6V wt% alloy coupons have exhibited target ICR values and low corrosion current densities under simulated aggressive PEMFC anode and cathode conditions, that are comparable to that of the nitrided Ni-(30-50)Cr wt% base alloys (see Table 1) [3-4]. The model Fe-27Cr-6V wt% alloy is not viable for stamped bipolar plates due to limited ductility, which result from the high level of Cr, and the potential

for sigma phase formation and embrittlement during thermal nitriding. The relatively high level of expensive V additions also increases the alloy cost. Therefore, work is underway to develop lower Cr and V containing Fe-base alloys that exhibit sufficient ductility to permit stamping and are low cost, yet still amenable to formation of a protective Cr-nitride base surface.

Results

A preliminary analysis of nitriding costs was performed by Brian James of Directed Technologies, Inc. in Fiscal Year 2008. Initial feedback was that DOE cost targets are potentially achievable at large volumes assuming a dwell time at the nitriding temperature on the order of 1-3 h. Efforts in FY 2009 were therefore focused on nitriding dwell time cycles of <3 h at 900-1,000°C. Foil form of 2205 stainless steel (Fe-22Cr-5Ni wt% base) and developmental Fe-20Cr-4V alloys were down selected for pre-oxidation/nitridation evaluation and single-cell fuel cell testing. Unlike earlier model sheet form alloys, which formed continuous Cr-nitride surfaces, the surfaces formed on the alloy foils using the short nitriding dwell times consisted of a mixed nitride/oxide structure (Figure 1). The Fe-20Cr-4V formed a Cr_2O_3

surface layer containing through-thickness V-nitride particles (Figure 1a). In contrast, regions of continuous Cr_2O_3 were observed on nitrided 2205 foil (Figure 1b), which resulted in locally unacceptable regions of high electrical resistivity. ICR and corrosion evaluation (Table 1) indicated significant improvement of the pre-oxidation/nitridation properties relative to as-received stainless steel foils (no surface modification treatment); however, the values were not as good as those previously achieved with the model materials that formed continuous Cr-nitride surfaces. In particular, ICR was moderately higher both pre- and post-corrosion testing. There was also some run-to-run ICR scatter, especially for the pre-oxidized/nitrided 2205 foil

Single-cell fuel cell testing was conducted with a test cycle of open-circuit voltage for 1 min, 0.60 V for 30 min, 0.70 V for 20 min, and 0.50 V for 20 min using a 50 micron high-performance MEA. The best short term V-I performance curves were exhibited by pre-oxidized/nitrided Fe-20Cr-4V, which was moderately better than untreated 904L stainless steel (highly alloyed stainless steel benchmark based on Fe-25Ni-20Cr-5Mo wt%) and machined graphite (Figure 2a). (It is speculated that the graphite plate V-I performance behavior was moderately lower due to minor differences between the machined graphite and stamped stainless steel flow fields.) The stamped and pre-oxidized/nitrided 2205 foils exhibited

FIGURE 1. High angle annular dark field scanning transmission electron microscopy cross-section of pre-oxidized and nitrided Fe-20Cr-4V (a) and 2205 (b) stainless steel foils.

FIGURE 2. Single-Cell fuel cell test V-I curves. a) initial performance; b) performance of 1,000⁺ h aged plates using a fresh MEA.

poor behavior (Figure 2a), which was attributed to regions of continuous Cr_2O_3 formed in the surface, and were dropped from the test matrix. Stamped plate/MEA integration design issues resulted in MEA failure at gas inlet/outlet regions after only 50-100 h of operation for all materials evaluated (not related to bipolar plate materials effects). This issue was resolved by switching to thicker 175 micron MEAs for durability testing, with a final performance check made with fresh 50 micron MEAs using the aged test plates/foils.

Over 1,000 h of single-cell fuel cell testing was accomplished for the stamped and pre-oxidized/nitrided Fe-20Cr-4V foils and benchmark graphite plates. No degradation in V-I performance curves was observed for the thicker 175 micron MEA. Figure 2b shows the final evaluation of the 1,000⁺ h aged plates with a fresh 50 micron MEA. The V-I curves for the graphite were essentially identical to the initial curves obtained with fresh graphite plates. A very slight performance decline was noted in the V-I data for the stamped and pre-oxidized/nitrided Fe-20Cr-4V, and this difference may be within the range of run-to-run variation. Post-test visual examination of the stamped and pre-oxidized/nitrided Fe-20Cr-4V foils (Figure 3) showed no evidence of corrosion attack (some slight staining and carbon deposition from the MEA was observed- analysis of the post-test surface is planned). Analysis of the 175 micron MEAs from the 1,000 h durability tests indicated levels of Fe contamination of only $0.1\text{--}0.3 \times 10^{-6} \text{ g/cm}^2$ for both the stamped and pre-oxidized/nitrided Fe-20Cr-4V and graphite plates. (No Cr or V was detected.) This level of Fe contamination is in the range of the fresh MEA starting levels and indicates excellent resistance to metal ion dissolution by the stamped and nitrided Fe-20Cr-4V foil.

Conclusions and Future Directions

The findings to date indicate good promise for the stamped and pre-oxidized/nitrided Fe-20Cr-4V foils as a bipolar plate material. Efforts in FY 2010 will focus on:

- Reduced nitriding cost and improving performance using rapid nitriding cycles with quartz/plasma lamps.
- Teaming with a fuel cell equipment manufacturer for manufacturability assessment (stamping and welding) and extensive fuel cell testing.

FY 2009 Publications/Presentations

1. M.P. Brady, H. Wang, J.A. Turner, H.M. Meyer, K.L. More, P.F. Tortorelli, and B. McCarthy, "Pre-Oxidized and Nitrided Stainless Steel Foil for Proton Exchange Membrane Fuel Cell Bipolar Plates: Part 1 Corrosion, Interfacial Contact Resistance, and Surface Structure" to be submitted to Journal of Power Sources 2009.
2. T.J. Toops, M.P. Brady, F. Garzon, T. Rockward, J. Pihl, P.F. Tortorelli, D. Gervasio, and F. Estevez, "Pre-Oxidized and Nitrided Stainless Steel Foil for Proton Exchange Membrane Fuel Cell Bipolar Plates: Part 2 Single-Cell Fuel Cell Evaluation" to be submitted to Journal of Power Sources 2009.

References

1. M.P. Brady, K. Weisbrod, I. Paulauskas, R.A. Buchanan, K.L. More, H. Wang, M. Wilson, F. Garzon, L.R. Walker, "Preferential Thermal Nitridation to Form Pin-Hole Free Cr-Nitrides to Protect Proton Exchange Membrane Fuel Cell Metallic Bipolar Plates", *Scripta Materialia*, 50(7) pp.1017-1022 (2004).
2. M.P. Brady, H. Wang, B. Yang, J.A. Turner, M. Bordignon, R. Molins, M. Abd Elhamid, L. Lipp, L.R. Walker, "Growth of Cr-Nitrides on Commercial Ni-Cr and Fe-Cr Base Alloys to Protect PEMFC Bipolar Plates", *International Journal of Hydrogen Energy*, 32, 3778 (2007).
3. M.P. Brady, B. Yang, H. Wang, J.A. Turner, K.L. More, M. Wilson, and F. Garzon, "Formation of Protective Nitride Surfaces for PEM Fuel Cell Metallic Bipolar Plates", *JOM- Journal of Metals, Minerals, and Materials Society*, 58, 50 August 2006.
4. B. Yang, M.P. Brady, H. Wang, J.A. Turner, K.L. More, D.J. Young, P.F. Tortorelli, E.A. Payzant, and L.R. Walker, "Growth of Cr-Nitride Surfaces to Protect Stainless Steels for Proton Exchange Membrane Fuel Cell Bipolar Plates", *Journal of Power Sources*, 174, 228 (2007).
5. H.L. Wang and J.A. Turner, "Ferritic stainless steels as bipolar plate material for polymer electrolyte membrane fuel cells", *Journal of Power Sources*, 128, 193 (2004).
6. H. Wang, M.P. Brady, K.L. More, H.M. Meyer, and J.A. Turner, "Thermally Nitrided Stainless Steels for Polymer Electrolyte Membrane Fuel Cell Bipolar Plates: Part 2: Beneficial Modification of Passive Layer on AISI446", *Journal of Power Sources* 138, 75 (2004).

FIGURE 3. Macrographs of cathode-side stamped and pre-oxidized/nitrided Fe-20Cr-4V test foils as-nitrided and after 730 and 1,050 h of single-cell fuel cell testing.

V.G.2 Next Generation Bipolar Plates for Automotive PEM Fuel Cells

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Contract Number: DE-FC36-07GO17012

Subcontractors:

- Ballard Power Systems, Vancouver, Canada
- Huntsman Advanced Materials, Woodlands, TX
- Case Western Reserve University (CWRU), Cleveland, OH

Project Start Date: March 1, 2007

Project End Date: August 31, 2009

Objectives

- Develop an expanded graphite/polymer composite to meet the 120°C fuel cell operating temperature target.
- Demonstrate manufacturing capability of new materials to a reduced bipolar plate thickness of 1.6 mm.
- Manufacture high-temperature flow field plates for full-scale testing.
- Validate performance of new plates under automotive conditions using a short (10-cell) stack.
- Show viability of \$5/kW cost target through the use of low-cost materials amenable to high volume manufacturing.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program

Multi-Year Research, Development and Demonstration Plan [1]:

(A) Durability

- Improved corrosion resistance

(B) Cost

- Lower material and production costs
- Increased power density due to decreased thickness
- Decrease weight and volume

(C) Performance

- Improved gas impermeability
- Improved electrical and thermal conductivity

Technical Targets

The goal of this work is to develop bipolar plates for polymer electrolyte membrane (PEM) fuel cells which will meet the high temperature performance and low cost manufacturing targets for 2010 and beyond. The targets are listed in Table 1. These goals will be met through a low cost manufacturing process based on expanded graphite technology and the high temperature performance of a new class of resins.

TABLE 1. DOE Technical Targets: Bipolar Plates (Table 3.4.14. [1])

Characteristic	Units	2010/2015	Program 2009 Status
Cost ^a	\$/kW	5/3	TBD
Weight	kg/kW	<0.4	0.57
H ₂ permeation flux	cm ³ sec ⁻¹ cm ⁻² @ 80°C, 3 atm (equivalent to <0.1 mA/cm ²)	<2 x 10 ⁶	TBD
Corrosion	μA/cm ²	<1 ^b	<1 ^b
Electrical conductivity	S/cm	>100	>1,000
Resistivity ^c	Ohm-cm	0.01	<0.01
Flexural Strength	MPa	>25	>55
Flexibility	% deflection at mid-span	3 to 5	TBD

^a Based on 2002 dollars and costs projected to high volume production (500,000 stacks per year).

^b May have to be as low as 1 nA/cm if all corrosion product ions remain in ionomer for metal plates. Corrosion of flexible graphite plates is not an issue.

^c Includes contact resistance.

^d Developers have used ASTM C-651-91 using four point loading at room temperature.

TBD – to be determined

Accomplishments

- New resin impregnated flexible graphite composite systems have been shown to have equivalent or improved dimensional stability and mechanical and thermal properties over the current GRAFCELL¹® composite.
- Gas impermeability has been demonstrated to a single plate thickness of less than 0.8 mm.
- Critical processing parameters for plate embossing have been identified and optimized.
- Single cell testing of machined resin-flexible graphite composite plates has demonstrated >1,100 hours of operation at 120°C with no evidence of plate degradation.
- Leachate, and glycol testing results do not indicate any significant problems with cell operations at elevated temperature.
- Bipolar plates have been pressed, cured, glued, leak tested and shipped to Ballard for stack testing.
- A short 10-cell stack of full-sized plates has been assembled and 1,000-hour testing at elevated temperatures initiated.
- Preliminary results on studies of high speed forming for resin impregnated bipolar plate production are positive.
- Cost analysis of the bipolar plate manufacturing process by Directed Technologies, Inc. is in progress.

Introduction

PEM fuel cells that can operate at higher temperatures can deliver more power and have a more efficient balance-of-plant. Accordingly, the 2010 Department of Energy targets for membrane and balance-of-plant components call for fuel cells that can operate at temperatures up to 120°C. Today's plate materials are typically used and tested at temperatures between 80 and 90°C. Although excellent performance has been demonstrated by fuel cells operating under these conditions in cars and buses around the world, vehicle manufacturers are already demanding higher operating temperatures to increase power and efficiency. It is clear that new bipolar plate materials must be developed that can meet DOE's targets for cost, corrosion, and other characteristics, as well as operate at higher temperature.

¹ GRAFCELL is a registered trademark of GrafTech International Holdings Inc.

Approach

In this project, a continuous expanded natural graphite structure will incorporate new thermoset resin systems that can improve the high temperature performance and properties of PEM fuel cells. Physical properties of resin-flexible graphite composite materials will be measured, and flow field plates of the composites will be evaluated in high temperature (120°C) single cell testing. Full-size automotive plates of the preferred composite will be molded and tested in a 10-cell stack under automotive conditions. A material and manufacturing cost estimate will be completed to show how the new bipolar plate composite can meet the DOE 2010 cost target for bipolar plates of \$5 per kW.

The use of polybenzoxazine polymers, a new class of resin system with higher glass transition temperatures, will be explored to provide the necessary improvement in high-temperature performance. Other bipolar plate physical properties will be addressed by further modification and formulation of the new resin system. Forming of bipolar plates from the new composites depends primarily on the resin-flexible graphite composite, but also on specific processing conditions of the forming method and on the design and geometry of the part. Aspects of the molding operation will be investigated through the use of small scale die sets. Ballard Power will supply specific geometric features pertinent to automotive-style bipolar plates, and these will be molded on a small scale to understand the processing limitations of the new resin-flexible graphite material. A full-scale die set will be made to mold bipolar plates for a 1,000-hour stack test at Ballard Power.

Results

The project plan consists of eight major tasks, the first three of which were completed and reported in the previous annual report. Tasks four through six were completed in the past year. The major accomplishments of each of the tasks are summarized in the following sections.

Task 1: Natural Graphite Selection (Completed in 2008)

Natural graphite sources from a number of domestic and international suppliers were evaluated. The selected samples were characterized using a standard regimen of raw material tests. Evaluation of the selected graphites was done using a design of experiments methodology to identify the working range of intercalation chemistries and exfoliation methods. Based on the results three graphite mats, G1, G2 and G3 were down-selected for preliminary composite evaluation in Task 3.

Task 2: Resin Identification and Selection (Completed in 2008)

Fuel cell performance characteristics, and resin specifications based on these characteristics, were defined. Using the resin specifications, a number of benzoxazine and epoxy resin systems that are potentially capable of meeting the project goals were identified, formulated, and samples were evaluated on the laboratory-scale. Based on the results of the evaluation, three resin systems were down-selected for further evaluation in composites with the expanded graphite mats selected in Task 1.

Task 3: Small-Scale Composite Preparation and Evaluation (Completed in 2008)

Resin-impregnated expanded graphite composites from the three expanded graphite mats and three down-selected resin systems were prepared. Cured resin expanded graphite composites were fabricated as blank stock with a target thickness of 0.60 mm. Two resin systems, 2G and 2H, were selected for additional evaluation. Dynamic mechanical analysis of the composites showed glass transition temperatures $>250^{\circ}\text{C}$; well in excess of the target 120°C operating temperature.

Composites of the two down-selected resin expanded graphite flat stock were temperature cycled in an environmental chamber using modified United States Council for Automotive Research - III Test Protocols for normal cycling and thermal shock cycle. Results of the mechanical testing on these samples were compared to the results obtained on samples which were not environmentally cycled. Analysis of the data shows that composites prepared with the 2G resin were statistically identical to or better than, the unexposed samples for all properties evaluated. However, the 2H resin system composites did show mechanical property degradation.

Statistically designed experiments were completed to determine the effects of key process parameters on preparation of the flexible graphite resin composites. Nitrogen and helium leak testing of the flat composite stock showed no detectable leaks for any of the un-embossed sheets under all combinations of process parameters tested. Final optimum processing conditions were determined as part of the embossing designed experiments in Task 4.

Task 4: Machining and Embossment of Small-Scale Composites (Completed in 2009)

Mechanical testing samples were prepared, analyzed, and compared to results from comparable samples consisting of the incumbent GRAFCELL Flow Field Plate (FFP) standard resin composite system. Samples were analyzed in an environmental

chamber at temperatures of -40 , 23 , 100 , and 120°C in 50% relative humidity (RH). Statistical analysis of the mechanical testing results indicates that the flexural and tensile strengths and work-of-fracture of the 2G and 2H benzoxazine resin systems were not significantly different from each other. However, comparisons of results between each resin system and the incumbent GRAFCELL FFP composite system indicate that both the benzoxazine resins are similar to, or indicate that both benzoxazine resins are similar to or significantly higher than the GrafCell composite at all temperatures tested in terms of flexural strength, modulus, and work-of-fracture. The improvements are most pronounced at elevated temperatures (100 and 120°C) where both benzoxazine resin systems are significantly stronger than the incumbent material and have significantly higher modulus (see Figure 1).

Additional physical and electrical property measurements have been made on the new benzoxazine resin systems composites. The measurements are summarized in Table 2 and are compared to similar results for the GRAFCELL FFP material where available. In general, physical properties on the new resin composites are similar to each other and comparable to or better than those of the GRAFCELL FFP composite system.

Using a proprietary oxidant flow field die pattern, plates were molded from the composite materials. Figure 2 is a photo micrograph of a cross-section of one of the flow field plate channels showing the feature definition possible with the new resin-flexible graphite composites. Nitrogen gas permeability, in-plane and through-plane electrical resistance, and dimensional processing changes (growth factors) were measured for each plate. Nitrogen gas permeability results indicated that either of the two benzoxazine resins systems could be successfully fabricated into full-size flow field plates that can survive the short stack testing that is planned for Tasks 6 and 7. With these results, the project contingency point was satisfied.

FIGURE 1. Mechanical Strength Testing Results

TABLE 2. Composite Property Comparison

Property	Method	Units	FFP Average	2G Resin Average	2H Resin Average
Bulk Density	ASTM C611	g/cm ³	1.68	1.68	1.72
Thermal Conductivity (x,y)	ASTM D5470 Modified	W/m-K	275	286	294
Thermal Conductivity (z)	ASTM C714	W/m-K	4.67	4.03	4.03
Thermal Diffusivity	ASTM C714	cm ² /s	0.039	0.033	0.033
Electrical Resistivity (x,y)	ASTM C611	μΩm	7.8	8	11
Electrical Resistivity (x,y)	GTI Internal	μΩm	NA	10	9
Electrical Resistivity (z)	GTI Internal, 1-Ply	μΩm	NA	934	937
Contact Resistance	GTI Internal	μΩcm ²	NA	2.1	3.0
Electrical Conductivity (x,y)	GTI Internal	S/cm	1470	1002	1111
Electrical Conductivity (z)	GTI Internal, 1-Ply	S/cm	NA	10.7	10.7
Thermal Expansion Coefficient (x,y)	ASTM E1545	μm/m-K	1.31	0.95	0.98
Thermal Expansion Coefficient (z)	ASTM E1545	μm/m-K	97.2	81.8	74.1
Flexural Strength, -40 °C	ASTM D790	MPa	63.9	67.3	69.0
Flexural Strength, 23 °C	ASTM D790	MPa	57.5	58.7	61.8
Flexural Strength, 100 °C	ASTM D790	MPa	37.8	47.8	51.3
Flexural Strength, 120 °C	ASTM D790	MPa	NM	44.3	49.7
Tensile Strength, -40°C	ASTM D638	MPa	41.9	41.3	44.6
Tensile Strength, 23°C	ASTM D638	MPa	38.6	37.4	43.8
Tensile Strength, 100°C	ASTM D638	MPa	29.2	32.8	36.4
Tensile Strength, 120°C	ASTM D638	MPa	NM	32.6	37.4
NA - Not Available					
NM - Not Measured

FIGURE 2. Test Tool Plate Cross Section

Task 5: Single Cell Testing (Completed in 2009)

High temperature cell components were identified and procured from a proprietary source by Professor Tom Zawodzinski of CWRU. The single cell testing protocol used more severe conditions than standard procedures, including potential cycling between 0.5 V, 0.8 V and open circuit voltage. The final single cell testing protocol was as follows: 114 hrs @ 80°C (70% RH); 86 hrs @ 120°C (24% RH). Cells were constructed using E-TEK 1500 gas diffusion layer; conditioned 24-48 hrs @ 80°C and liquid samples were collected throughout operations. Cell resistance was as follows: 0.23 Ohm cm² after 114 hrs @ 80°C;

0.55 Ohm cm² after 71 hrs @ 120°C; and 0.54 Ohm cm² after 86 hrs @ 120°C.

Single cell testing of the 2G resin flexible graphite composite is complete. As was anticipated, periodic disassembly of the cell, inspection of the flow field plates and replacement of the membrane electrode assembly (MEA) was necessary. There was no evidence of degradation or contamination of the composite after more than 1,120 hrs of operation at 120°C. Similar testing was initiated for the 2H resin composite and over 200 hrs of operation were completed with no evidence of plate degradation. Unfortunately, additional testing of the 2H plates was suspended due to consumption of the supply of high temperature MEAs. Additional MEAs could not be obtained and the decision was made to discontinue any additional single cell testing. Analysis of the effluent that was collected during testing is in progress.

Task 6: Design and Manufacture Full-size Bipolar Plates (Completed in 2009)

Ballard selected an FFP design based on a modification of a plate from a previous design for use in final full-size plate production. This modified plate design has a plate assembly thickness below 1.6 mm and a plate area greater than 250 cm² which meet the project requirements.

The final selection of graphite and resin for full sized plate fabrication was made and consisted of the 2G benzoxazine resin system and G3 graphite. The 2G

resin-composite demonstrated better performance than the 2H resin composite in a significant majority of the evaluation criteria. The final graphite selection was based primarily on flake availability. Using the selected starting materials, approximately 60 fuel and 60 oxidant plates were fabricated. All of the plates were within the target thickness of <0.8 mm and with length and width measurements within Ballard's specifications.

Task 7: Short Stack Test of Full-Size Plates (In progress)

In a change from the original project plan, GrafTech was responsible for gluing the individual flow field plates to form the bipolar plate. The new glue dispensing equipment was delivered, installed and used to glue the anode and cathode plates and end-plate assemblies. All the glued assemblies were successfully cured.

Using the initial GTI shipment of bipolar plates, Ballard assembled one 10-cell stack and started testing in early June. The stack developed problems with cell six at higher temperatures and was taken off-test and disassembled. Preliminary evaluation indicated that the problem with the cell was due to degradation of the MEA seals at high temperatures. A modified seal capable of operation at higher temperatures was substituted and the stack operating temperature reduced to 110°C. The stack is in the process of being reassembled and tested. Two additional stacks will be assembled; one for testing by a group at Argonne National Laboratory and the second for freeze testing by Ballard. The Argonne group was selected by the DOE to perform verification of the bipolar plates.

Task 8: Economic Assessment of New Technologies (In Progress)

Bipolar plate manufacturing cost analysis of the new resin systems and associated processes has been initiated. Costs of raw materials and production processes for the anticipated manufacturing processes have been obtained or estimated. To ensure consistency with previous bipolar plate manufacturing cost estimates, the DOE has requested that the manufacturing cost estimate is made using the methodology employed by Directed Technologies, Inc. (DTI). DTI has been contacted, a non-disclosure agreement executed, and cost data exchanged.

Conclusions and Future Directions

Conclusions

The following are conclusions based on the work completed to date.

- New expanded graphite-resin composite systems have superior thermal stability and equivalent or

improved dimensional stability and mechanical properties over the current GRAFCELL composite.

- Gas impermeability for these materials has been demonstrated to a single plate thickness of less than 0.8 mm which is adequate for fuel cell operation under the proposed design.
- Preliminary leachate, glycol and single cell testing results on the new composite systems are positive or do not indicate any significant problems with cell operations at elevated temperature.
- Critical processing parameters for plate embossing have been identified, optimized and full size bipolar plates embossed, sealed and glued.
- A short 10-cell stack has been assembled and placed in test using a standard duty cycle.
- Manufacturing cost analysis data has been obtained and submitted to DTI for evaluation.

Future Directions

- Complete durability testing targeting 1,000 hours on a 10-cell stack.
- Conduct freeze start testing.
- Post test analysis, results and review including plate inspection.
- Assembly and delivery of a full size 10-plate stack to Argonne National Laboratory.

Special Recognitions & Awards/Patents Issued

1. "Fuelling Great Opportunities: Resin Development Program for Fuel Cell Applications", JEC Composites Raw Materials Award and presentation, Paris France, March 2009.

FY 2009 Publications/Presentations

1. "Flexible Graphite-Resin Composite Bipolar Plates for High Temperature High Energy Density PEM Fuel Cells", Fuel Cell Symposium Presentation #: 1481.
2. Oral presentation before the members of the Department of Energy and the FreedomCAR and Fuel Partnership's Fuel Cell Technology Team (FCTT) on November 20, 2008,

References

1. "Hydrogen, Fuel Cells and Infrastructure Technologies Multi-Year Research, Development and Demonstration Plan", U.S. Department of Energy, Hydrogen, Fuel Cells & Infrastructure Technologies Program, DOE/GO-102003-1741, Oct 2007.

V.G.3 Low Cost Durable Seals for PEMFCs

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Contract Number: DE-FG36-07GO17005

Subcontractors:

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- Henkel Corporation, Rocky Hill, CT
- Virginia Polytechnic Institute and State University (Virginia Tech), Blacksburg, VA

Project Start Date: April 1, 2007

Project End Date: September 30, 2009

Technical Targets

The aim of this project is to develop and evaluate new non-silicone liquid injection moldable (LIM) and dispensable materials to improve durability for both transportation and stationary applications while maintaining or improving on the cost benefits of LIM silicone materials (Table 1).

TABLE 1. DOE Targets Receiving Focus as Part of this Project

Characteristic	Units	2009 Status	2010 / 2011 ^a
Durability	hours	> 10,000 hours achieved ^b	5,000/40,000
Sealability at Low Temperature	°C	Testing to-date indicates success	-40/-35
Cost ^c	\$/kW _{net}	To be evaluated	(2.00 – 3.88) ^d

^a DOE Transportation/Stationary targets

^b Real-time out-of-cell testing at 90°C

^c Based on high volume production (500,000 transportation systems per year/2,000 stationary units per year). **Note:** A cost target for seals is not currently carried in the Hydrogen, Fuel Cells & Infrastructure Technologies Program Multi-Year Research, Development, and Demonstration Plan. See footnote (d) below for an explanation of how this target was derived.

^d Suggested cost target range for transportation applications derived from Reference 1 (\$3.88/kW), Reference 2 (\$2.00/kW) and conversations with the Fuel Cell Tech Team (\$2.00/kW). Based on Reference 1, a reasonable suggested target for stationary applications may be \$6.03/kW.

Objectives

- Develop a working material specification to guide the development of proton exchange membrane fuel cell (PEMFC) seal materials.
- Synthesize and compound materials that meet the requirements of the materials specification.
- Evaluate candidate materials through accelerated ex situ testing to predict whether the material will meet durability objectives given in Table 1.
- Validate the performance of the best performing material candidate through in-cell testing.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

(A) Durability

Accomplishments

- Completed more than 10,000 hours of out-of-cell testing at 90°C.
- Completed more than 4,500 hours of out-of-cell testing at 120°C.
- Developed a new material candidate that is expected to have greater high temperature stability.
- Began comparisons against other materials previously used or being considered for use.

Introduction

Seal durability is critical to achieving the 2010 DOE operational life goals for both stationary and transportation PEMFC stacks. The seal material must be chemically and mechanically stable in an environment consisting of aggressive operating temperatures, humidified gases, and acidic membranes. The seal must also be producible at low cost. Currently-used seal materials do not meet all these requirements.

High consistency hydrocarbon rubber compounds that show promise for compatibility with the PEMFC environment are difficult to process in a way that leads to low cost PEMFC production. Silicone-based LIM rubber compounds which are easy to process in ways leading to low-cost production are highly gas permeable and have been shown to be unstable in PEMFC applications. To produce PEMFC stacks which are both highly durable and low in cost, a seal material with the stability of high consistency hydrocarbon rubber and the processing ease of a LIM silicone is sought.

Approach

To accomplish the objectives of this project, the approach is to develop and evaluate non-silicone LIM seal materials that can meet the specialized mechanical, compatibility, and cost requirements inherent to the design and operation of PEMFCs. To guide material development, a working material specification was developed. Materials developed to this specification by Henkel are evaluated through out-of-cell testing at Virginia Tech, Henkel and UTC Power in simulated environments. Using an appropriate set of accelerated testing techniques, an initial lifetime estimate will be made for the candidate materials. The best candidate or candidates will be selected for in-cell testing to validate the performance of the material in a PEMFC environment. Specimens for out-of-cell testing and full size prototypes for in-cell testing are produced by Freudenberg-NOK General Partnership.

The outcome of the project will benefit the PEMFC industry by providing a seal material specification, a material that satisfies it, and verification that the specification and the material enable a low-cost and durable seal.

Results

With the specification completed early in the project, the work over the last year has been focused on two primary tasks:

1. Synthesizing and formulating new materials for evaluation.
2. Out-of-cell material testing.

Additional material development experiments were conducted over the last year. The work has yielded another material candidate, FCS2, for evaluation. It is a one-part material with the cure characteristics of the two-part material evaluated earlier in the project. This new candidate is also designed to have improved high temperature stability.

This brings the total of material candidates evaluated to three. These materials have been given the designations FCS0, FCS1 and FCS2. Some key properties of the three are compared to each other and to the materials specification in Table 2. All three meet the minimum requirements in the material specification. This means that seal components suitable for use in PEMFC applications could be produced from

TABLE 2. Comparison of Key Properties for Three Candidates Evaluated To-Date

Henkel LIM Hydrocarbon Elastomer Property Table for DOE					
Properties	Project Requirements		FCS0	FCS1	FCS2
	Minimum	Ultimate			
Process Properties					
LIM processable	Yes	Yes	Yes	Yes	Yes
Viscosity @ room temperature (cPs)	<= 700,000	<= 600,000	~ 500,000	~ 543,000	~ 543,000
Mold temperature (°C)	< 135	<= 110	120 to 130	120 to 130	120 to 130
Mold time (second)	<= 400	<= 60	60 to 120*	60 to 120*	60 to 120*
Mechanical Properties					
Hardness (Shore A)	15 to 68	30 to 55	31	30	30
100% Modulus (Mpa)	0.25 to 3.5	1 to 2.5	0.75	0.68	0.69
Tensile strength (Mpa)	>= 0.5	>= 0.8	1.3	1.3	1.1
Elongatin (%)	> 125	> 150	163	171	160
Tear strength Die C (kN/m)	>= 2.7	>= 5.0	3.7	3.7	3.9
Environmental Requirements					
Temperature resistance (°C)	-40 to 85	-40 to 90	-40 to 90	-40 to 90	-40 to 120
Notes					
*cure schedule: 120 second in the mold @ 120°C and then 1 hour post cure @ 130°C

Green: meets minimum & ultimate requirements

Yellow: meets minimum requirements

Red: below minimum requirements

any of the three. Additional development continues. The next candidate, FCS3, is expected to meet the ultimate requirements of the specification. Meeting the ultimate requirements broadens the range of design options available. The material will also provide a step improvement in strength and elongation.

A variety of out-of-cell tests are being used in the evaluation of the materials being developed for this project. The aim is to evaluate the beginning of life properties and to evaluate how those properties change with time when subjected to combinations of temperatures and chemical environments typical of PEMFC operation. One of the most important measures for seals is compressive stress relaxation (CSR). This is a measure of the decay in sealing force with time. During the past year, over 10,000 hours of CSR testing was completed on the first material candidate evaluated for the project. The results are summarized in Figure 1. The test was run at 90°C in de-ionized water, a 50/50 water/ethylene glycol (EG) mix, and in air. The 50/50 water/EG mix had the greatest effect. However, the sealing force decay in all cases was less than 20%. This is a significant result. While significantly greater values can typically be accounted for in the design of sealing systems, lower values translate directly into increased durability and greater design flexibility. For reference, the sample was prepared in accordance with ASTM D 6147 Section 7.1.1.

Recognizing that there is still interest throughout the PEMFC industry, particularly in the automotive sector, to operate at temperatures as high as 120°C, CSR testing at 120°C was conducted on the second material evaluated for the project. The result is summarized in Figure 2. The test ran for 4,500 hours. Force decay at the end of the test was approximately 10%. A comparison of this

data to the 90°C air aging case in Figure 1 reveals that the force decay results are similar at 4,500 hours. This suggests that physical rather than chemical relaxation still dominates after 4,500 hours at 120°C.

As hydrocarbon-based elastomers, it is expected that one of the most significant threats to the stability of the candidate materials is oxidation. Based on this expected importance, a comparison of the oxidative stability to some other materials which have been considered for PEMFC applications was begun and is still underway. A key interim result of this work is provided in Figure 3. In this figure, relative change in mass with time is tracked for testing at 150°C. In this case, FCS1 is being compared to three ethylene propylene diene monomer (EPDM)-based materials. Significant changes in the

FIGURE 2. Results for CSR testing at 120°C in air. Approximately 10% load loss was observed at the end of the 4,500 hour test. This result taken in conjunction with the result from Figure 1 strongly suggest that material candidates being developed for this project will meet the 2010 DOE durability goals for automotive PEMFC applications.

FIGURE 1. Results for CSR testing at 90°C in three aging media. Less than 20% loss in sealing force was observed in 10,000 hours for all cases.

FIGURE 3. Comparison of EPDM and candidate material oxidative stability. The relative change in mass was tracked with time for three EPDM-based materials and FCS1, one of the developed candidate materials. The result indicates that FCS1 has higher oxidative stability.

rate of either weight gain or loss can be correlated to significant degradation in mechanical properties. The result indicates that the candidate material has greater oxidative stability than the EPDM-based materials tested. Several tests are also currently underway to compare the candidate materials to other materials such as silicone.

In addition to primary tasks discussed above, work on other tasks has also continued. Hundreds of sub-scale molded O-ring seals have been produced. The parts are seals over-molded around the perimeter of a disc of gas diffusion material. They are being used to determine appropriate molding parameters and to explore the role of geometry on load relaxation by comparison with results obtained from ASTM 6147 style samples. Some limited sub-scale molding was initiated and full-size mold flow analyses were conducted.

Conclusions and Future Directions

Based on the work performed to date for the project, the following can be concluded:

- The general material development strategy (synthesis and compounding) appears to be sound.
- Based on CSR, oxidation or other on-going testing, the materials developed have a high probability of success for meeting the 2010 DOE goals for use in automotive PEMFC applications.

Activities for the remainder of the project will include the following:

- Further development and evaluation of the next material candidate, FCS3.
- Molding and evaluation of seals over-molded around the perimeter of subscale membrane electrode assemblies (MEAs).
- Development of a high volume capable injection molding technique for over-molding seals around the perimeter of full-scale MEAs.
- Additional out-of-cell testing designed to validate test results obtained to date.
- Full-size in-cell testing to validate out-of-cell test results.

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V.H.1 CIRRUS: Cell Ice Regulation & Removal Upon Start-up

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Contract Number: DE-FG36-07GO17014

Subcontractors:

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- SGL Carbon, Meitingen, Germany
- University of Delaware, Newark, DE

Project Start Date: July 1, 2007

Project End Date: June 30, 2010

(D) Water Transport within the Stack

(G) Start-up and Shut-down Time and Energy/Transient Operation

Technical Targets

Nuvera is seeking to demonstrate the ability to achieve DOE's 2010 targets in a full format, subscale stack assembly operating in a simulated but fully realistic ambient environment, using system-compatible operating protocols.

In the first half of the project Nuvera has been striving to achieve the difficult target of a quick start (50% of rated power in 30 seconds or less) from a -20°C start condition, respecting the budget of 5 MJ of energy for the complete start-up and shutdown cycle. The hardware platform used in this work is Nuvera's Andromeda™ fuel cell – this particular fuel cell design was realized first in 2005 and has been substantially validated over the past four years. Andromeda™ has an active area of 360 cm² and a rating current density of 1.0 A/cm².

Over the last year Nuvera succeeded in demonstrating the capability of the current technology to meet, and exceed, the target in realistic conditions, as illustrated in Figure 1, and as will be described below.

Thermal analyses and operating experience indicate that the thermal mass of Andromeda™ will likely prevent the technology from meeting the -40°C startability target. In order to accomplish the extreme low temperature start goal, Nuvera has conceived, designed, and prototyped a new stack technology named Orion™. The Orion™ platform has a rating current density of 2 A/cm², and

Objectives

The objective of the CIRRUS project is to advance the state of the art in fuel cell operability under subfreezing conditions, consistent with requirements for applications involving such conditions (e.g. automotive, forklifts, backup power systems, and auxiliary power units) and DOE targets, specifically to:

- Demonstrate repeatably, ability to achieve 50% rated power in less than 30 seconds from a -20°C start condition, using less than 5 MJ auxiliary energy.
- Demonstrate unassisted start capability from an initial temperature of -40°C.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

FIGURE 1. Freeze Start of Andromeda™ Stack from -20°C Meeting DOE Target

will exploit higher current density operation to achieve increased power density and reduced thermal mass, with the objective of enabling operation from -40°C.

Accomplishments

- Installed and commissioned a climatic chamber that maintains stack ambient environment and reactant gases to -20°C during testing, to ensure test conditions simulate real-world operating conditions.
- Reduced stack freezing time from 8 hours to 60 minutes to enable significantly increased testing throughput
- Optimized shutdown protocol to achieve a 75% reduction in shutdown time (in preparation for freeze start), from 8 minutes to 2 minutes.
- Achieved 50% of rated stack power in 18 seconds from a -20°C starting temperature, using 3.3 MJ of energy (34% less than target).
- Fabricated and conducted preliminary testing of the proof-of-concept Orion™ stack.

Introduction

For fuel cells to be commercially viable as powerplants in automotive applications, the ability to survive and start reliably in cold climates (as low as -40°C) is a must. Since fuel cells are water-based energy systems, this requirement is a significant technical challenge.

Water transport studies are imperative for achieving DOE targets for fuel cell startup time from subfreezing conditions. Stack components must be selected that endure thermal and humidity cycling over the operating range, and operating strategies must be devised that enable the fuel cell to start, i.e. generate power and heat up sufficiently before ice extinguishes the galvanic reactions, and afford evacuation of a sufficient amount of water, using a limited amount of auxiliary power, at shutdown.

Approach

Nuvera has structured the project into four different phases: investigation, selection, qualification and validation. In the investigation phase (Q3 and Q4 2007, completed) Nuvera surveyed the state-of-the-art on the topic and developed the “enabling tools” to execute the project (test infrastructure and modeling capabilities). In the following selection phase (2008, completed) Nuvera used such tools to select a proper freeze start strategy to meet the DOE requirements and a set of material to enable the successful execution of the test. Nuvera is currently in the qualification

phase (2009) in which the performance stability of the material set and operating methods is being assessed in a durability test campaign. The results of this campaign, supported by the interaction with the partners of the project (W.L Gore, SGL and University of Delaware) will identify improvements to be pursued through one or more iterations of materials, strategy and stack architecture. The effectiveness of these actions will be verified in the validation phase (Q1 and Q2 2010) in which the most advanced configuration will be tested and the improvements will be quantified.

Results

Since the last reporting period, Nuvera has worked to increase the level of realism in its testing procedure and dramatically decrease the energy budget consumed to achieve the startup.

Facilitated by a new climatic chamber, freeze start testing is performed with the stack frozen in a controlled environment at -20°C. Moreover the reactant gases pass through dedicated heat exchangers that cool them down before they reach the stack. The previous setup controlled only the temperature of stack (-20°C), and the test was performed at room temperature.

Nuvera recognized in the early phases of the project the importance of applying an effective purging procedure prior to shut down in a cold condition to minimize the amount of water that could potentially freeze. Formerly the anode and cathode compartments were purged with constant flows of, respectively, hydrogen and air. On a real system a constant flow of H₂ on anode side can only be achieved with a recirculation pump that adds cost to the system and the increases the energy used to perform the procedure on account of its inefficiency. In light of this, the purging strategy has been changed and currently is based on a high pressure (4 bar absolute max), instantaneous purge of H₂ that can be achieved through a proper set of valves. This new approach enabled a significant reduction of the energy consumed for this purpose (from 3.9 MJ to 0.45 MJ, as reported in Table 1).

The startup procedure has also been optimized, adopting a steeper ramp of current. This approach accelerates heat production, preventing the water produced in the reaction from freezing and blocking the active sites.

The combination of these two improvements has enabled a successful startup from -20°C exceeding the 2010 targets both in terms of time to 50% power (18 seconds vs. 30 seconds) and energy consumption (3.3 MJ vs 5.0 MJ).

The process of optimizing the startup strategy has itself represented an endurance test: Figure 2 shows the cell voltage over 100 successive freeze starts performed

TABLE 1. Contributions to Energy Consumption Calculation

Energy consumed during Shutdown...	
Air compressor parasitic (LHV of H ₂ consumed to power compressor during purging phase)	0.564 MJ
H₂ wasted in purges (LHV of H ₂ vented or burned)	0.450 MJ
Energy consumed during Startup...	
H₂ used during startup (LHV of H ₂ consumed to produce electric power in first 30 sec)	2.292 MJ
TOTAL	3.306 MJ*

*It was 5.6 MJ in Fiscal Year 2008, 26 MJ in FY 2007, H₂ at startup was not considered.

LHV - lower heating value

to tune the strategy. These results confirm that the stack can survive in the short run. More diligence is needed to assess and understand decay modes associated with the start/stop strategy, and accordingly drive the development of more suitable materials. In this endeavor, Nuvera engaged the proton exchange membrane fuel cell community in an intensive workshop (February 20, 2009) dedicated to the freeze topic in which 38 participants from 22 different organizations came together to examine existing data and understand the main causes of degradation and the open issues that remain to be addressed.

Nuvera has actively advanced the design of the new Orion stack architecture that will enable a significant reduction of the thermal mass and corresponding startability at temperatures below -20°C. Nuvera has successfully assembled the first prototypes (example shown in Figure 3), that are meant to offer a proof of concept of the proposed architecture without requiring sophisticated and costly production tools. Early tests performed in standard operating conditions ($T > 0^\circ\text{C}$,

Procedure optimization process

FIGURE 2. Cell Voltage Profile over 100 Freeze Starts Performed to Optimize Startup Procedure **FIGURE 3.** Polarization Curve of Orion™ Stack (2 cells) in Low Pressure Conditions (open valve)

open valve operation on air compartment) have shown performances in line with the design point (see Figure 3), and offer an exciting preview of the results yet to come.

Conclusions and Future Directions

Nuvera recognizes the need to reduce stack thermal mass as a key strategy to accomplish the DOE target of startability from -40°C . Nuvera will continue developing Orion™, improving the quality of the prototypes and fine tuning the design features, to enable operation at temperatures below 0°C . Nuvera is confident of being able to perform a successful startup from extreme temperatures on the Orion™ technology in the validation phase.

In parallel, Nuvera is working on understanding the stability of the current freeze start method through a durability campaign based on two separate tests: (1) subjecting a non-operational stack to thermal cycling to evaluate the pure effect of temperature oscillation, and (2) repeated freeze start/shutdown cycle testing of a separate stack to capture the full phenomena. Subsequent to testing, the materials used will be subjected to diagnostic analysis in collaboration with partners to measure the extent of the degradation, and assess the causative factors. Such investigation will lead to a new generation of materials with an extended life.

FY 2009 Publications/Presentations

1. July 2008 - Detroit, MI - FreedomCar Review.
2. December 2008 - Las Vegas, NV - FC Performance and Durability Conference.
3. February 2009 - Billerica, MA - Presentation at PEMFC Workshop organized by Nuvera.
4. May 2009 - Crystal City, VA - 2009 DOE Hydrogen Program Merit Review (FC38).

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V.H.2 Development of Thermal and Water Management Systems for PEM Fuel Cells

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Contract Number: DE-FC36-03G013109

Project Start Date: December 2002

Projected End Date: December 2009

Objectives

- Develop an advanced heat exchanger (radiator) that can efficiently reject heat with a relatively small difference between fuel cell stack operating temperature and ambient air temperature.
- Test humidification systems to meet fuel cell inlet air humidity requirements. The moisture from the fuel cell outlet air is transferred to inlet air, thus eliminating the need for an outside water source.
- Test the selected humidification system at sub-ambient conditions.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Multi-year Research, Development and Demonstration Plan:

(E) System Thermal and Water Management

The technical targets for this project are listed in Table 1.

TABLE 1. Technical Targets

Characteristics	Units	Target	Honeywell Status
Humidity of PEM cell stack inlet air	% at 80°C	>60	TBD
Cooling requirements with 85°C coolant temperature and flow rate of 2.5 kg/sec, with frontal area not to exceed 0.32 sq meter	kW	50	50
Radiator cost (by TIAX LLC) without markup	\$	56*	60
Reliability of radiator	hrs	5,000	TBD
Total parasitic power (air fan + cooling pump)	kW	<2.4	TBD

TBD – to be determined

*Cost based on 80 kW fuel cell system

Accomplishments

- Thermal Management
 - The radiators performance model was validated by four sub-scale radiators test data.
 - Full-scale radiators with louver and microchannel fins were built and tested.
- Water Management
 - The humidity system test stand was modified to meet the high air flow and humidity test requirements. The testing of test articles is underway.
 - The enthalpy wheel was modified by the supplier to eliminate high seal leakage rate.
 - The supplier for a planer membrane-based humidity device was identified and the testing is scheduled for later this year.

Introduction

Balance of plant components of a proton exchange membrane (PEM) fuel cell automotive system represents a significant portion of total cost based on the 2008 study (Direct Hydrogen PEMFC Manufacturing Cost Estimated for Automotive Application) by TIAX LLC, Cambridge, MA. The objectives of this thermal and water management (TWM) project are twofold:

- Develop an advanced cooling system to meet the fuel cell cooling requirements. The heat generated by the fuel cell stack is a low-quality heat (low temperature) that needs to be dissipated to the ambient air. To minimize size, weight, and cost of the radiator, advanced fin configurations were evaluated.
- Evaluate air humidification systems which can meet the fuel cell stack inlet air humidity requirements. Two humidification devices were down-selected, one based on membrane and the other based on rotating enthalpy wheel. The sub-scale units for both of these devices have been successfully tested by the suppliers.

Approach

To develop a high-performance radiator for a fuel cell automobile, various advanced surfaces were evaluated, including foam; advanced, offset, and slit louver fins; and microchannel with various fin densities. A value function was developed to evaluate and compare the cost of various fin geometry radiators. The value function was based on the cooling system weight, performance, parasitic power, and initial cost. Two fin geometries – 18 fins per inch (fpi) louver and 40 fpi microchannel – were down-selected. The full-scale radiators were built and tested to validate the performance.

After extensive literature search and evaluation of existing humidification devices, two humidification systems were down-selected for TWM fuel cell applications: a Nafion® membrane-based system and enthalpy wheel-based system. Most of the humidification systems currently in use by HVAC (heating, ventilation and air conditioning), food, and chemical industries utilize low operating and differential pressure devices. The subscale units for the two selected devices were successfully tested at the supplier laboratories, meeting the fuel cell (FC) humidity requirements. A full-scale Nafion® membrane module and enthalpy wheel was designed, built and is being tested to validate the performance. A test stand was designed and built, to test the selected humidification devices where FC stack operating conditions are simulated. The testing at ambient conditions is scheduled in Fiscal Year 2009 and the sub-ambient testing will follow in FY 2010.

Results

Thermal Management

Two full-scale radiators with 18 fpi louver and 40 fpi microchannel radiators were built and tested. The size of each unit was 27.6" wide, 17.7" high, and 1.3" deep, as shown in Figure 1.

FIGURE 1. Full-scale radiators with 18 fpi louver and 40 fpi microchannel aluminum fins.

Air-side effectiveness and pressure drop test data for the full-scale 18 fpi louver fin radiator is plotted against the performance model prediction in Figure 2. The test data for air-side effectiveness and pressure drop is in good agreement with model prediction. In Figure 3 the data for the full-scale 40 fpi microchannel fin radiator is plotted. The test data is also in good agreement with the performance model data.

After detailed analysis of the four sub-scale radiator test data, the two finalists based on value functions were the 18 fpi louver and 40 fpi microchannel. The sub-scale test data validated the performance model. The value function for the four sub-scale radiators based on the test data is shown in Figure 4. The 18 fpi louver and 40 fpi microchannel show the lower values within the radiator maximum allowable thickness of 2.75 in. The value function for the full-scale radiator is being generated, which will determine the optimum fin configuration.

FIGURE 2. The test data for the full scale 18 fpi louver fin radiator plotted against performance model prediction with coolant flow rate of 32 gallons per minute.

FIGURE 3. The test data for the full scale 40 fpi microchannel fin radiator plotted against performance model prediction with coolant flow rate of 35 gallons per minute.

FIGURE 4. Value function is plotted against the radiator thickness for all four sub-scale radiators. The maximum allowable thickness of the automobile radiator is 2.75 inches. Based on sub-scale data the 40 fpi microchannel radiator has the best value for FC automobile applications.

The humidity system test stand was modified to be able to operate at higher air flow and humidity conditions. During the test stand modification additional sensors were added to improve the measurement accuracy. High air leakage across the enthalpy wheel seal was observed during low air flow testing, as previously reported. The unit sealing system was modified by the supplier. The testing of the selected humidification devices is expected to be complete by the mid 2010.

Conclusions and Future Directions

The testing of two full-scale radiators sized for a FC automobile was completed. Both units meets the cooling requirements, however the final selection will be based on the results of the value function analysis. Based on sub-scale data, the 40 fpi microchannel radiator has the best value for FC automobile application.

The selected radiator performance data will also be used by Argonne National Laboratory to validate the FC automotive system model. A final report will be submitted, which will conclude the thermal management portion of this project.

The testing of the enthalpy wheel, full- and half-scale membrane module is underway. A planer-based membrane module has been evaluated for FC application. The rectangular configuration will be beneficial from an installation point of view. A supplier of planer membrane-based humidification devices has been identified who is designing a full-scale unit to meet FC humidification performance requirements. This full-scale unit will be tested in the existing test stand. The humidification device down-selected will be tested at sub-ambient conditions. The completion of this testing will conclude the water management portion of this project by mid-FY 2010.

FY 2009 Publications/Presentations

1. 2009 Hydrogen Program and Vehicle Technologies Program; Annual Merit Review and Peer Evaluation Meeting – Washington, D.C. – May 2009. Presentation FC#39.

V.I.1 Development and Demonstration of a New-Generation High Efficiency 1-10 kW Stationary Fuel Cell System

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Contract Number: DE-FG36-07GO17013

Project Start Date: July 28, 2007
Project End Date: July 28, 2010

- Electrical energy efficiency @ rated power – 40%
- CHP energy efficiency @ rated power – 80%
- Cost – \$750/kW (in volume production)
- Durability – 40,000 hours lifetime

Forecasted project progress toward meeting DOE targets is shown in Table 1.

TABLE 1. Progress Toward DOE Targets

Target ¹	2009 ²	2010	2011	2012 ³
Electrical Efficiency @ Rated Power	30-35	35-37	37-38	>38
CHP Energy Efficiency @ Rated Power	70	75	80	>85
Cost (\$/kW)	\$400/kW			
Durability (hours)	1,000	2,000	5,000	>10,000

¹ Table values are projections based on modeling work done by IE

² To be validated experimentally in September 2009

³ Depends largely on successful development and system integration of adsorption-enhanced reforming

Objectives

The objectives of this project are to identify and seek out methods to facilitate overcoming specific challenges related to the development of fuel cell technologies and their deployment for commercial use in combined heat and power (CHP) applications.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan are:

- (A) Durability
- (B) Cost
- (C) Performance

Technical Targets

This project is developing novel fuel processing, polymer electrolyte membrane (PEM) fuel cell technologies and integration strategies in order to help achieve DOE targets for integrated stationary PEM fuel cell power systems for year 2011. These targets are:

Accomplishments

- Extended run (513 hours) of small scale reformer that consistently yielded ~65% thermal efficiency while undergoing 53 thermal cycles.
- Completed the design of a TRL 4 (component and/or breadboard validation in a laboratory environment) fully integrated CHP system using IE's PEM fuel cell and hydrogen generation technology platforms.
- Developed a novel coating for IE's bi-polar fuel cell plate, improved diffuser materials and catalyst optimization that in combination have boosted stack efficiency by 3% more than levels achieved in 2008.
- >1,000 hours fuel cell system run time demonstrated in lab trials.

Introduction

The development of highly efficient and cost-effective clean energy solutions is not without challenge. The maturation of hydrogen fuel cell technologies is expected to become a significant player in reducing our dependence on imported fossil fuels and help curb the creation of greenhouse gases.

This project is directed at designing a stationary CHP system using a PEM-based hydrogen fuel cell that will provide residential and light commercial end-users with on-site generated electrical and heating needs. The proposed technology approach combines a chemical reactor (reformer) and purifier that convert either a liquid or gaseous hydrocarbon feedstock such as natural gas, into hydrogen that is then fed into the fuel cell where a reaction between hydrogen and oxygen produces electrical power in a non-combustion reaction. This reaction in turn generates an electric current and heat is recovered from this exothermic process. The parallel focus on adsorption enhanced reforming (simultaneous reforming and removal of CO₂) may lead to the enabling technology that promises greater efficiencies and lower capital costs than conventional reforming.

Approach

The approach used to develop the new-generation 1-10 kWe CHP unit that achieves high efficiency, long durability and low cost targets simultaneously includes a bold optimization and integration of existing IE technology platforms. The CHP unit will be based on IE's open architecture integration philosophy that maintains a high purity hydrogen interface between the hydrogen generation and fuel cell subsystems. The fuel cell subsystem will be derived from IE's existing 2 kW CHP platform and its advanced 10 kW evaporatively-cooled fuel cell that achieves 60% gross efficiency on pure hydrogen. An innovative hydrogen generation subsystem will be developed by leveraging IE's Phase 1 experience into a newly redesigned 10 kWe steam reformer (SR) and integrated fast cycle pressure swing adsorption (PSA) off-gas purifier. This hydrogen generation platform currently achieves thermal efficiencies in the ~63-68% range. In parallel, IE has been investigating an adsorption-enhanced reformer (AER), that when modeled using simulation software, suggest possible efficiencies of 75-80%.

The approach depends on achieving an optimized balance between increased stack performance (high cell voltage at high current densities), low cost cell components, hydrogen generation efficiency (high fuel conversion, lower steam/carbon ratios, maximum recuperation of heat and water vapor, and high hydrogen recovery), low parasitic power components, efficient grid-connected inverter and lowest cost balance of plant.

Results

Accomplishments to date include the following:

Fuel Processor Development

After completing the design and build of a new SR, the vessel was tested both with and without being

integrated into the PSA. The high pressure core reactor was then examined after completing 513 hours of hot operation and deemed to have maintained (by visual inspection) its mechanical integrity. Being that the reformer was subjected to several thermal cycles without serious damage, this suggests that the basic design may indeed be a good candidate for further ruggedization with the potential to be long-lived (see Figure 1).

Data collected during the reformer testing shows that repeatable efficiencies of ~65% were achieved.

FIGURE 1. Hydrogen Generator Testing

TABLE 2. Hydrogen Generator Experimental Efficiencies

Date and Time	Feed CH ₄ (SLPM)	Supplemental CH ₄ (SLPM)	Total CH ₄ (SLPM)	Produced H ₂ (SLPM)	Efficiency LHV (%)
9/24/2008 16:27	69.5	0	69.5	151	65.2
9/24/2008 17:29	69.4	0	69.4	150	64.9
9/30/2008 17:11	69.8	5.3	75.1	164	65.5
10/1/2008 11:20	69.5	5.3	74.8	163	65.7
10/1/2008 13:30	70	0	70	153	65.9
10/1/2008 15:00	61	4.6	65.6	142	65.2
10/22/2008 11:04	70	5	75	162	65.1
10/22/2008 16:00	60.7	6	66.7	145	65.3
10/22/2008 17:40	62	7	69	150	65.3

LHV - lower heating value

Table 2 shows these results from tests during the months from September to October 2008.

AER

The work on adsorption enhanced reforming is continuing at California Polytechnic University Pomona (CPP) under the direction of professors Dr. Winny Dong and Dr. Vilupanur Ravi. A four-tube AER reactor has been designed and constructed in preparation of testing during July-August 2009. The rig is configured to produce hydrogen continuously. These tests will be conducted using liquid ethanol as the feed. Simulation models conducted previously by Sandia National Laboratories suggest that if the AER system engineering proves successful, a CHP system fuel-to-electric efficiency may approach 48%. Feasibility data using a potassium-promoted hydrotalcite adsorbent with the AER approach were submitted in report last year's Fiscal Year 2008 annual report. Figure 2 shows the new test rig at CPP. The heated reactor tubes are within a furnace in the center of the photograph with the gas delivery and programmable logic controller equipment on the left side.

FIGURE 2. AER Test Rig

Fuel Cell

Continued improvements including the use of new diffuser materials, catalyst optimization and the use of novel bipolar coating materials resulted in an increase from 0.56 to 0.7 V @ 0.5 A/cm² thus resulting in a 2-3% uplift of efficiency over results obtained in 2008.

CHP

During FY 2009, a fully integrated CHP system has been designed. Based on heat and materials balances, a complete set of engineering documents have been created including process flow diagrams, piping and instrumentation diagrams, bills of materials and mechanical models for the entire system and its 23 related subsystems. Construction of this CHP prototype is underway and substantial progress has been made. The system will be using a Matlab/Simulink automated controller which has been coded for remote monitoring of system performance with controlled safety related shutdowns and alarm sequences. Shakedown testing is scheduled for September 2009. Figure 3 shows a high level prototype CHP system under development.

Conclusions and Future Directions

FY 2009 has culminated with significant progress with regard to the integrated design of both the fuel cell and reforming technology platforms into a CHP system. Validation testing will begin in September and provide

FIGURE 3. CHP Prototype Mechanical Drawing

valuable data for consideration into a field-deployable system that will go through the cost engineering marking process. Afterwards, the unit will be installed and commissioned within a European Union nation during 2010. In order to work toward higher efficiencies, FY 2010 will bring additional focus on developing the AER technology and optimization of balance-of-plant components. Major tasks/direction going forward include:

- Engage potential system packaging/manufacturing partners.
- Complete deployable system design verification documentation.
- Evaluate alternate PSA technologies.
- Design/build rotary valve to enable system integration/testing of AER.
- Install and field-commission a 10 kWe CHP system.

Special Recognitions & Awards/Patents Issued

1. Woods, Richard R.; Porter, Brooks F.; Durai-Swamy, K.; October 21st, 2008, United States Patent # 7439273, "Hydrogen Purification Process and System"

FY 2009 Publications/Presentations

1. 2009 DOE Annual Merit Review-Washington, DC, May 20th, 2009. Presentation FC 25.
2. 2009 ASME 7th International Fuel Cell Science, Engineering & Technology Conference-Newport Beach, CA, July 7th, 2009. "Low-Cost, High Efficiency Distributed Hydrogen Production for CHP".
3. Li, Mingheng, Equilibrium Calculation of Gaseous Reactive systems with Simultaneous Species Adsorption, Journal of Industrial and Engineering Chemistry, Res. 2008, 47, 9263-9271.

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1. Development of 50 kW Fuel Processor for Stationary Fuel Cell Applications, Stevens, et al., Chevron, 2007, Final Report, DE-FC36-03GO13102.
2. Sircar, et al., I&EC Res., 46, 5003-5014 (2007)] and one in press [J. Hydrogen Energy, 33 (2008)].
3. Sircar, S., Kratz, W.C.: Simultaneous production of hydrogen and carbon dioxide from steam reformer off-gas by pressure swing adsorption. Sep. Sci. Technol. 23, 2397-2415 (1988).
4. Sircar, S., Hufton, J.R., Nataraj, S.: Process and apparatus for the production of hydrogen by steam reforming of hydrocarbon. U.S. Patent No 6,103,143 (2000).

V.I.2 PEM Fuel Cell Powerplant Development and Verification

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Contract Number: DE-FC36-04-GO14053

Project Start Date: January 2, 2004

Project End Date: December 31, 2009

Objectives

- Evaluate the operation of a 150 kW natural gas-fueled proton exchange membrane (PEM) fuel cell.
- Assess the market and opportunity for utilization of waste heat from a PEM fuel cell.
- Verify the durability and reliability of low-cost PEM fuel cell stack components.
- Design and evaluate an advanced 5 kW PEM system.
- Conduct demonstrations of PEM technology with various fueling scenarios.
- Evaluate the interconnection of the demonstration 5 kW powerplants with the electric grid.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (B) Cost
- (A) Durability
- (G) Start-up and Shut-down Time and Energy/Transient Operation

Technical Targets

Table 1 highlights the progress made toward the targets specified for fuel cell power plants on reformat in the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan. Additionally, Table 2 is a summary of the progress toward specific targets that are used as success metrics for the project.

TABLE 1. Progress Toward Meeting Technical Targets for Stationary Fuel Cell Power Plants Operation

Characteristic	Units	2011	2009 UTC Power Status
Electrical Energy Efficiency @ Rated Power	%	40	45% on H ₂ On Reformat: TBD
Durability @ <10% Rated Power Degradation	hours	40,000	>20,000 hours Cell Stack Assembly ~4,000 hours in power plant
Transient Response Time (for 10% to 90% of rated power)	seconds	1	<1
Survivability (min and max ambient temperature)	°C °C	-35 +40	-40 40

TBD - to be determined

Accomplishments

- Completed demonstration of >20,000 hours of cell stack operation.
- Completed the design and fabrication of a prototype advanced system that incorporates significant cost reduction technology and system simplification for improved reliability, efficiency and performance.
- Developed 5 kW advanced fuel cell power plant with >20% increase in volumetric power density that achieves parity with similar internal combustion-based power plants.
- Achieved ~4,000 hours of endurance testing on a baseline 5 kW system and 400 hours of testing on the advanced 5 kW system. The ultimate goal is 40,000 hours demonstrated in a field application.
- At initial volumes, the cost of the powerplant has been reduced by >30% including transient power and direct current (DC) regulation devices necessary for powerplant operation in a stationary application.
- Demonstrated alternating current (AC) output, parallel operation for "building block" approach for power scalability.

TABLE 2. Progress Toward Meeting Stationary Fuel Cell Program Metrics

Parameter	Metric	Demonstration	Result
Rating	5 kW, applicability up to 200 kW range power plants	Test (5 kW)	5 kW powerplant constructed with rated power up to 40°C @ 1,800 meters. Scalability in 5 kW building blocks feasible for AC and DC applications. Design is scalable to larger power applications
Efficiency	>35 %	Test	@ 5 kW net on Pure Hydrogen: Fuel Cell System without power conditioning: 51% Advanced system with power conditioning: 45%
Primary Fuel	Hydrogen from various sources including feasibility for hydrocarbon reformat	Test, Analysis	Study for natural gas, LPG, propane underway.
Emissions	As good as or better than U.S. requirements	Test	Zero emissions. Hydrogen concentration in exhaust is less than 25% LFL under all operating conditions. Not yet analyzed for reformer based system.
Operation	Start time < 30 minutes, All U.S. weather conditions	Test	Demonstrated start time is 15 seconds (Hydrogen based system). Not yet analyzed for reformer based system.
Durability	Design goal: ≥15,000 hrs (ultimate application goal >40,000 hr) Demonstrated requirement: 1,000 hrs, ≥1 year replacement interval	accelerated component and cell stack testing	5 kW baseline powerplant unit has accumulated ~4,000 hrs with <10 μV/hour of non-recoverable performance decay.
Mean Time Between Forced Outages	>2,000 hours with long term goal of 5,000 hours	Test, statistical analysis	Reliability model projects 1,800 hours and testing is ongoing to increase the projection.
Maintainability	Web based remote control, diagnostics	Test	Demonstrated remote monitoring, control with both modem or ethernet capability.
Use of thermal energy	Integration with liquid desiccant	Study	Completed
Grid Interconnectivity	Any U.S. grid with minimal equipment	Demonstration Test, UL 1741 assessment	AC 120 VAC single phase demonstrated AC grid connect inverter under development for demonstration in 2009.
High availability and multiple grid connections	Increased availability of power plants and demonstrated grid connections on feeder lines; suitability for backup power	Demonstration Test, modeling, and statistical	Baseline 5 kW powerplant demonstrated 99.6% availability over 1,500 hrs
<div> <div>COMPLETED</div> <div>On Target</div> <div>At risk</div> <div>Below target</div> </div>			LPG - liquefied petroleum gas LFL - Lower flammability limit

- Demonstrated an electrolyzer as an alternative fuel supply.

Introduction

This project continues to advance the development and demonstration of the fundamental technologies necessary to enable PEM stationary fuel cell power plants to meet the needs of commercial stationary power applications. This project will continue to demonstrate technology for low-cost, high durability stationary fuel cells using a 5 kW system platform to verify fundamental technologies in a complete system environment. The 5 kW platform is an efficient method to evaluate and build on lessons learned during early 150 kW power plant demonstration activities. This project continues to accomplish goals to further the development of fuel cell technology toward meeting the demands of stationary applications. Accomplishing these technological achievements will enable commercialization of fuel cells for stationary power applications.

Approach

The focus of this project is to demonstrate technology for low-cost, high durability stationary fuel cells using a 5 kW system platform to verify fundamental technologies in a complete system environment. The approach will focus on three levels of development:

- Fundamentals:** Development of fundamental technologies to close technical gaps needed for the commercial viability of fuel cells for stationary applications (i.e. cost, durability, performance and reliability).
- Advanced Power System Development:** The advanced 5 kW system will scale up technologies developed in the Fundamentals task as well as focus on cost reduction to close technical and commercial gaps.
- Demonstration:** The baseline and advanced 5 kW stationary power systems will be tested in lab and field settings to validate durability and performance targets are met as well as develop power system extensions necessary to adapt fuel cells for stationary applications (i.e. AC/DC output and grid interconnectivity, integration with various hydrogen sources, and scalability).

UTC Power will evaluate cost-effectiveness and durability of the PEM stationary power plant technologies and system design based on the demonstration results. This approach will enable a robust assessment at the integrated powerplant and sub-system (e.g., cell stack and fuel processor) levels.

Improved component technology will be deployed as lessons learned are accumulated that identify durability and reliability vulnerabilities.

Results

Fundamentals

Alternate low cost unitized electrode assembly (UEA):

- Internal resistance (IR), open circuit voltage (OCV), falloff time, and conductivity have exceeded project requirements.
- Performance at 1,000 mA/cm² is close to minimum criteria:
 - Some air sensitivity at high current densities after 1,000 hours. This will be monitored during endurance testing after installation in a power plant.

Table 3 summarizes the development progress to date for the low-cost UEA.

Advanced System

- System met power output, efficiency, and initial water balance test requirements.
- Endurance testing in progress (>400 load hours @ 5 kW, >100 start-stop cycles (Figures 1 and 2).

FIGURE 1. Advanced 5 kW System Undergoing Endurance Testing

FIGURE 2. Benchmarking Results of UTC Advanced 5 kW System's Power Density

TABLE 3. Summary of Alternate UEA Testing Results

Product	IR (mV/100 mAsc)	mV @ 1,000 mA/cm ²	OCV (mV)	Falloff Time (min)	Recoverable Decay (μV/hr)	Non Recoverable Decay (μV/hr)
5 kW PEM CSA Spec	< 15	600	898	> 1	< 70	< 21
Baseline UEA (30-Cell CSA)	13	628	945	4.7	457	
Alternate UEA-1 30 cell, 500 hrs	10.2	570	979	9.04	226	47
Alternate UEA-2	8	642	982	> 10	239	< 21 (682 Load hours)
33-Cell stack with Alternate UEA-2	12	654	> 970	7.9	616 (1,000 hrs)	29

CSA - cell stack assembly

Demonstrations

UTC 5 kW previously developed baseline power system endurance testing.

Testing completed under non-DOE program:

- Continued endurance hold at 2 kW net power until 2,500 hours.
- At 1,500 hours: Average efficiency = 42%, Availability = 99.6%.

Testing in progress under DOE project:

- ~4,000 load hours, and >450 start-stop cycles.

The advanced 5 kW system is based on the UTC baseline system and incorporates low cost cell stack assembly technology, improved power density, increased operating envelope and higher power conditioning efficiency. Field demos with the advanced system will be conducted with selected key end users and at the UTC Power facility to gain reliability data and field experience.

AC Demonstration:

- Parallel system designed and assembled with inverters, rectifiers, transfer switch and AC distribution monitor.
- AC output and parallel system operation testing was completed.

Flexible Fuel Source:

- Electrolyzer
 - Grid independent solution demonstrated.
 - Initial operation to 2,300 PSI without a compressor completed.
 - >1,000 hours runtime was achieved.
 - New membranes installed to enable 3,000 PSI hydrogen production.
- Reformer
 - Conceptual design initiated.
 - Fuel cell combined heat and power and reformer system undergoing testing.

Conclusions and Future Directions

With the accomplishments and progress toward technical goals, this project has made strides to close technical gaps. Continued emphasis on the development and scale up of technologies to improve durability, cost and performance will be necessary to make a fuel cell that meets all targets for commercial stationary applications:

Durability: >20,000 hours of cell stack assembly endurance will need to be validated through the scale up and demonstration in stationary fuel cell powerplant operation.

Cost: At initial volumes, the cost of the powerplant has been reduced by more than 30% including transient power and DC regulation devices necessary for powerplant operation in a stationary application. Continued focus on low-cost technology development and scale up for field demonstration will be a necessary step for determining commercial viability of the power plant in stationary applications. Performance and efficiencies are being improved; however, additional work will be necessary to verify performance and efficiencies on fuel from reformers and alternative fuel sources.

FY 2009 Publications/Presentations

1. 2009 DOE Hydrogen Program Review – Washington, D.C. - May, 2009. Presentation FC#26.

V.I.3 Intergovernmental Stationary Fuel Cell System Demonstration

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Contract Number: DE-FG36-07GO17017

Subcontractors:

- Construction Engineering Research Laboratory (CERL), Champlain, IL
- Ballard Power Systems, Burnaby, British Columbia, Canada
- Keyspan (National Grid), Brooklyn, NY

Project Start Date: October 1, 2007

Project End Date: April 30, 2010

Objectives

To design and produce an advanced prototype proton exchange membrane (PEM) fuel cell system with the following features:

- 5 kW net electric output.
- Flex fuel capable – liquefied petroleum gas (LPG), natural gas, ethanol.
- Reduced material and production cost and increased durability.
- Increased electrical efficiency over the current alpha design.
- Increased total efficiency by incorporating combined heat and power (CHP) capability.

To show a path to meet long-term DOE objectives:

- 40% system electrical efficiency.
- 40,000-hour system/fuel cell stack life.
- \$750/kW integrated system cost (with reformer).

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section (3.4.4) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) Durability
- (B) Cost
- (C) Performance

Technical Targets

Integrated Stationary PEM Fuel Cell Power Systems (5-250 kW) Operating on Reformate

This project is conducting fundamental analysis and demonstration of fuel flexible (ethanol/LPG) CHP integrated system. Results of the current system design have shown the ability to meet the following DOE 2011 targets:

- Survivability (min and max ambient temperature) -35 to +40°C
 - Successful system operation shown from -40 to +46°C
- Noise: <55 dB(A) @ 10 m
 - Measured noise emissions of <60 dB(A) at 3 m at rated power at nominal ambient conditions which when applying the inverse square law equals 49.5 dB(A) at 10 m.

Learning gained from work activities of this project will be applied toward the design and manufacture of a system that is on a path to meet the following DOE 2011 targets:

- Durability @ <10% rated power degradation: 40,000 hours
- Cost @ 2,000 units/year: \$750/kW_e
- Performance (Target values adjusted to account for LPG-fueled system.)
 - Electrical Efficiency @ rated power: 38.5%
 - CHP efficiency @ rated power: 78.5%

Accomplishments

- Completed design and analysis tasks necessary to define the components of the system. Prototypical hardware was procured and tested to ensure their capability to meet system requirements.
- Completed system concept design review in June 2008.

- Completed the tasks necessary for the integrated prototype system design including computer-aided design (CAD) modeling, design documentation, bill of materials (BOM) creation, and system integration (Figure 1).
- Completed system detail design review in November 2008.
- Completed the build of prototype system shown in Figure 2.
- Began system integration testing including system controls development and parameter optimization for steady-state and transient operating modes. A sample system response chart is shown in Figure 3.
- Commenced site planning and preparation for system installation at the CERL electrolyzer laboratory in Champaign, Illinois (Figure 4).

Introduction

Long-term commercial acceptance of PEM-based fuel cell systems is contingent on reducing the material and operating costs and improving the durability of the

FIGURE 1. Evolution of System Design

system and its components. The current technologies employed for PEM fuel cell stacks and the uniqueness of other system components contribute significantly to the material cost of the system.

This project will not only advance the state-of-the-art of PEM fuel cell technologies, but will also establish an integrated, low-cost, flex fuel reformer for on-site fuel cell power generation. These achievements, in turn, will help to enable commercialization of the technology by improving economic feasibility and providing multiple fuel options for a variety of commercial applications. This project will include the design, manufacture, test and field demonstration of a CHP, grid-connected fuel cell system. The resulting system will advance the state-of-the-art toward the Department of Energy's program objectives of increased durability, reduced cost, and improved efficiency.

FIGURE 2. System Fabrication and Assembly

FIGURE 3. Prototype System Operation

FIGURE 4. Installation Site Planning

Approach

To achieve these objectives Plug Power will use experience in systems engineering and integration gained from over 600 systems installed and operated worldwide to perform concept development and detail design of an ethanol/LPG flex fuel capable fuel cell system that incorporates new technologies necessary to advance toward meeting the DOE 2011 targets for durability, cost and performance.

Results

During the past year Plug Power has completed simulation and modeling of 168 design iterations to optimize system performance and generate component design requirements. The system consists of Plug Power's fourth generation autothermal reformer to generate fuel for a PEM-based fuel cell stack which is coupled with power conditioning equipment to provide regulated alternating current to the end user. The hardware necessary to satisfy this system architecture was sourced and a statistically significant sample of all components was testing to prove their capability of meeting requirements. The project successfully passed

a system concept design review in June 2008. A CAD model of the full prototype system was created and the documentation necessary to source the chosen components was created. The components were integrated into a prototype system design and the BOM based on this design was created to perform analysis necessary to project the unit cost in production volumes. The project passed a detailed system design review with DOE personnel in November of 2008. No issues were found and the project entered the build phase. A functional prototype of the design was built at Plug Power's Latham facility in March 2009. During the build, the assembly procedures and system BOM were verified. Once assembled the prototype began system integration testing to validate functionality. Automated system controls were developed to operate each subsystem and the control parameters were optimized for both steady-state and transient operating modes. Further controls optimization work is still to be done but the system has shown capabilities of efficiency of 32%, approximately 5 points higher than prior vintages of the design as shown in Figure 5.

The planning necessary to install the system at the CERL facility in Champaign, Illinois was started

FIGURE 5. Efficiency Comparison

in February of 2009. Once installed the system will provide electric power and heat for CERL's electrolyzer laboratory. Also in the past year the focus of the project has been narrowed to focus only on using LPG feedstock for the reformer. This decision was based on feedback from reviewers received at the annual project review in 2008, and the results of the previous year's work on this project which uncovered economic and logistical challenges of using ethanol as a feedstock. A request was made and accepted by DOE during the September 2008 program review to focus solely on LPG as a fuel for the prototype system installation at CERL.

Conclusions and Future Directions

As a result of activities of this past year Plug Power was able to design and build a prototype fuel cell system which shows good progress toward meeting DOE's 2011 goals. Successful system operation has been achieved and the work necessary to show that the resulting production design is commercially viable has been completed. Planning is underway for the prototype system to be installed and commissioned at the CERL facility later this year.

For the remainder of the project we have defined the following tasks necessary to bring this project to a successful conclusion.

- Remainder of 2009:
 - Complete design verification testing.
 - Conduct field readiness review.
 - Complete site planning and system installation.
 - Commission prototype system and commence field operation and support.
- Fiscal Year 2010:
 - Complete field operation and support.
 - Decommission system.
 - Post demonstration testing.
 - Project close out.

V.I.4 FC40 International Stationary Fuel Cell Demonstration

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Contract Number: DE-FG36-07GO17016

Subcontractor:

BASF Fuel Cell ETEK, Somerset, NJ

Project Start Date: May 2007

Project End Date: April 2009

Objectives

Develop, test and validate a high-temperature proton exchange membrane (PEM), stationary, reformate-based, combined heat and power (CHP), fuel cell system as the first demonstration of a modular, scalable design for a worldwide market.

- Design a system with a total cost of <\$750 kW in production volumes.
- Achieve electrical efficiencies of 35% (with line of sight to 40%) and overall system efficiencies of 85%.
- Demonstrate robustness that would lead to a 40,000-hour system life.
- Develop modular and scaleable system and CHP hydraulics concepts.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

(A) Durability

(B) Cost

(C) Performance

Technical Targets

This project is directed at the development of a micro-CHP PEM, stationary fuel cell system. It will advance the state-of-the-art of high-temperature PEM fuel cell technologies, and use this technology to address the following DOE technical targets as outlined in Table 1.

TABLE 1. Progress towards Meeting Technical Targets for Integrated Stationary PEM Fuel Cell Power Systems (5-250 kW) Operating on Reformate

Characteristic	Units	2011 Target	Plug Power 2009 Status
Electrical energy efficiency @ rated power	%	40	30
CHP, energy efficiency @ rated power	%	80	85
Cost	\$/kWe	750	2,000
Transient response time (from 10% to 90% power)	seconds	<3	300
Cold start-up time (to rated power @ - 20°C ambient)	minutes	<30	not applicable
Continuous use application			(indoor application)
Survivability (min and max ambient temperature)	°C °C	-35 +40	not applicable
Durability @ <10% rated power degradation	hours	40,000	4,000
Noise	dB(A)	<55 @ 10 m	<55 @ 10 m
Emissions (combined NOx, CO, SOx, hydrocarbon, particulates)	g/1,000 kWh	<1.5	not tested

Accomplishments

- Developed an improved membrane electrode assembly (MEA) cathode electrode which is more resistant to corrosion and is robust to load cycling.
- Improved stack design and stack component manufacturing processes that will lead to better performance and life.
- Developed an inverter that is two points higher in efficiency and is half the size and weight of the previous design.

- Integrated advanced technologies into a compact system design ready for commercial development.
- Built and commissioned three systems in the U.S., Germany and the Netherlands.
- Tested systems against real world applications achieving 30% electrical, 85% thermal efficiencies, 30 minute startup and load following capability.
- Achieved over 3,000 hours testing in three installations generating significant learning and opportunity for continued development under the project.

Introduction

Plug Power Inc. (Plug Power) executed an international development and demonstration project within the framework of the existing European Union (EU)–U.S. Cooperation Agreement on fuel cells. The design, test and validation of a micro-CHP PEM, stationary fuel cell system advanced the state-of-the-art of high-temperature PEM fuel cell technologies and is bringing a domestic fuel cell heating appliance system design one step closer to commercialization.

Approach

Plug Power and BASF have conducted eight years of development work prior to this project, demonstrating the potential of polybenzimidazole membranes to exceed many DOE technical targets. The approach taken to fulfill the requirements of this project was to identify and develop of key enabling technologies and integrate them into a system architecture capable of meeting the needs of a commercial customer. These technologies and this architecture were demonstrated in operational systems in the U.S. and the EU. The major tasks associated with this project are:

- The development of a worldwide system architecture.
- Stack and balance of plant module development.
- Development of an improved, lower cost MEA electrode.
- Receipt of an improved MEA from the EU consortium.
- Integration of modules into a system.
- Delivery of system to EU consortium for additional integration of technologies and testing.

Results

In the past year, the focus of the extended team has been the downselection of key technologies for integration into the final system design, the detailed

system design itself and parts procurement, system build and debug. The most significant technology initiatives have been centered on the high-temperature MEA, the stack and system power electronics.

MEA improvement efforts were focused on improving the cathode electrode in order to make it more resistant to oxidation and robust to load cycling. The basis for creating more stable supported catalysts lies in the choice of carbon support. A number of carbon supports were tested for corrosion resistance and the best selected (see Figure 1).

Numerous alloys of Pt were prepared containing Co, Ni, Fe, Vn, and Cr, or ternary combinations thereof. In the course of this task three potential graphitic supports were identified and two were selected for use as catalyst supports. Two supports were developed and the numerous catalysts were downselected to a field of three: Pt alloy(I) on Carbon 1, Pt alloy(I) on Carbon 2, and Pt alloy(II) on Carbon 1. These three candidates were passed to the electrode development team for

FIGURE 1. Carbon Support Selection and Pt Alloy Performance for MEA Cathode Electrode

optimization. After tradeoff studies, Pt alloy(II) on Carbon 1 was incorporated into the scale up of full-sized MEAs.

Stack initiative efforts were concentrated on analysis and design improvements for increased performance and life. Of particular importance are single-pass versus double-pass anode flow fields and stack compression tolerance stack-up.

Prior to this project, the design team had concluded that a “two-pass” orientation offered the highest anode utilization (1.1 – 1.2 stoichiometry target) and the highest stack efficiency. This has not proven to be the case with the testing of manufactured plates. It is currently believed that while this is thermodynamically correct, the manufacturing tolerances required to maintain a two-pass orientation cannot be held with the current material and design. On reformat, the anode stoichiometry impact begins to be observable when operating below 1.8. At 1.8 anode stoichiometry, the difference between 1-pass and 2-pass was about 13 mV and at 1.4 anode stoichiometry the difference increased to 80 mV (see Figure 2).

It is currently understood that for optimum MEA performance in the high-temperature stack, a nominal cell compression of 20% +/- 5% must be maintained (per BASF's recommendations). The stack components that determine cell compression are plate pocket depth, MEA thickness, and viton insulator height. The assigned nominal values and associated tolerances of these components must work together to keep the MEA compression within the allowable range (15% - 25%).

Currently, all components have been found to be outside of their tolerance specifications to maintain compression on the MEA to within BASF's recommendations. The results of this study are being shared with the suppliers in order to leverage work towards improving the nominal and distribution of the

FIGURE 2. Reformate Anode Stoichiometry Sensitivity Comparison Between 1-Pass and 2-Pass

insulator height. See Figure 3 as a sample result of a stack component compression analysis.

A new transformerless inverter platform was developed and evaluated. The inverter module consists of the inverter card, inductor and heat sink. The stand alone inverter module used for testing is shown below in Figure 4.

Each module was tested for basic functionality and then sub-systems were tested for efficiency with the result that the new design is approximately 2 points higher in efficiency than its predecessor.

The team then built and debugged three systems: “E1”, “E2” and “E3” and installed them in Plug Power, Latham labs, Plug Power, Apeldoorn, Netherlands labs and Vaillant, Remscheid, Germany labs.

On its way to commissioning in the Netherlands, system E2 was displayed at the Hannover Fair in Hannover, Germany in April where it was well received by industry and academia (see Figure 5).

FIGURE 3. Sample Average MEA Compression Distribution

FIGURE 4. Inverter Performance Improvements

After commissioning, the systems were used for controls development and for testing against high level customer requirements. Under test the systems demonstrated 30% electrical efficiency, over 85% thermal efficiency and a 30 minute start-up.

With limited controls development under the project, the team was able to achieve rudimentary load following under simulated operating conditions. The system was able to achieve full-load conditions from zero watts net output in under three minutes. A 1 kilowatt load change could easily be achieved in under 1 minute. Load following is critical to the value proposition of a CHP device and allows the fuel cell appliance to maximize the return on investment by the customer (see Figures 6 and 7).

Finally, the systems were run in continuous power mode to understand life issues and reliability. Under the project, the systems achieved over 3,000 operating hours with 1,500 of them in Vaillant labs (see Figure 8). This testing generated data for additional controls development and reliability improvements.

FIGURE 5. Built, Debugged and Displayed Three Systems

FIGURE 6. Demonstrated 30-Minute Start-up

This information is invaluable to the team as it moves forward to commercialize this technology in the United States and Europe.

Conclusions and Future Directions

High-temperature PEM fuel cell systems promise to be a commercially viable technology for micro-CHP, residential and light commercial applications. Much refinement in the areas of manufacturing and supply chain development are required, but the core technology is ready to begin the commercialization process. The following work is planned outside of the project:

- Complete controls development.
- Install systems in employee homes.
- Complete new design with updates from testing.

FIGURE 7. Demonstrated Load Following

Experienced
international
installation team:

FIGURE 8. Installation and Commissioning at Vaillant in Remscheid, Germany

- Commission reliability fleet.
- Begin field trials.

FY 2009 Publications/Presentations

1. 2009 DOE Hydrogen Program Review – Washington, D.C. – June, 2009. Presentation FC40.

V.I.5 Development of a Low Cost 3-10 kW Tubular SOFC Power System

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Contract Number: DE-FC36-03NT41838

Project Start Date: April 1, 2008
Project End Date: September 30, 2011

desired product while also demonstrating required life and efficiency targets through multi-level testing.

TABLE 1. Progress Towards Meeting Technical Targets for Stationary Fuel Cell Power Generators

Characteristic	Units	2011 Goal	2009 Status
Electrical Efficiency	%	40	33
Combined Heat & Power Efficiency	%	80	84
Durability @ <10% Rated Power Degradation	hours	40,000	7,000
Cold Start-Up Time	minutes	<30	<45
Transient Response (from 10-90%)	seconds	<3	<10
Cost	\$/kWe	\$750	\$729 (estimate on volume)

Objectives

The goal of this project is to develop a low-cost 3-10 kW solid oxide fuel cell (SOFC) power generator capable of meeting multiple market applications. This is accomplished by:

- Improving cell power and stability.
- Cost reduction of cell manufacturing.
- Increase stack and system efficiency.
- Prototype testing to meet system efficiency and stability goals.
- Integration to a micro-combined heat and power (mCHP) platform.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) Durability
- (B) Cost
- (C) Performance

Technical Targets

This project is directed toward achieving the stationary generation goals of the DOE fuel cell power systems. This project will work on cost reduction of the

Accomplishments

- Reduced cell thermal cycle degradation to <1%/100 thermal cycles from 20-30% to meet DOE stability and life objectives.
- Have reduced cell stack size by 82% and volume by over 75%.
- Have proven stack stability with purge less operation meeting needs of mCHP product requirement.
- Have achieved over 43% electrical efficiency (gross power/lower heating value natural gas) on latest stack technology.

Introduction

Achieving combined heat and power goals of over 40% net electrical efficiency and over 80% total energy efficiency are goals of the Department of Energy and present administration to reduce our dependence on foreign energy and reduce the emission of greenhouse gases. SOFCs, with their ability to use the present U.S. fuel infrastructure and high grade waste heat are ideal candidates for this challenge. To date, the limitation on making this goal a reality has been the reliability and cost of such systems.

This project is designed to address these limitations and bring this promising technology to the market place. This is being achieved by working on all aspects

of the SOFC power generator including: (1) improving cell power and stability, (2) reducing cost of cell manufacture, (3) increasing stack and system efficiency, (4) prototype system testing, (5) and integration into a mCHP platform. This phase of the project will make a major drive toward the DOE's goals set forth for 2011 stationary power generators.

Approach

To achieve the project objectives, the approach has been to perfect the individual system pieces followed by optimizing their integration through:

- Cell Technology: Improving power and stability of the cell building block.
- Cell Manufacturing: Improving processing yield and productivity while decreasing material consumption.
- Stack Technology: Refining stack assembly and improve integrity while cost reducing individual component costs.
- System Performance: Developing simplified controls and balance-of-plant components to allow for a reliable, highly efficient unit.

Results

In the past year, the focus has been on stabilizing the present cell technology and reducing the cost of this part while integrating it in the present generator design. Prior to this year, the performance and the stability of the individual cell tube were very good at steady-state operation but improvements in thermal cycle capabilities were needed. Work focused on identifying the root causes for degradation on thermal cycles which was ultimately reduced to the anode-cathode interconnection. Contact to the chromite interface was being weakened or broken on thermal cycles and was not able to reattach on subsequent heatups. Once the root cause was identified, a number of different techniques were trialed to determine what gave the best stability. Figure 1 shows the voltage of the cell under load for subsequent thermal cycles to over 450 cycles. The baseline design had a loss of greater than 10%/100 thermal cycles where the final method chosen and placed into production resulted in less than a 1%/100 thermal cycle loss.

Work also focused on cost reduction for manufacturing of the individual cells. A number of processes were automated as well as reductions made in material usage. The manufacture of the tube was converted from an extrusion process to an isopressing operation. Isopressing allows significant advantages including higher volume throughput, reduced scrap, and integration of a hemispherical closed end. Introduction of this process also allowed for the manufacture and testing of tubes with decreasing amounts of wall

FIGURE 1. Single Cell Thermal Cycle Capability

FIGURE 2. Comparison of Standard and 45% Thinner Walled Tube

thickness. Since the tube represents over 90% of the total mass of the fuel cell, decreases in its wall thickness have a direct bearing on weight and cost. Figure 2 shows a picture of a 45% reduced wall thickness tube versus a standard tube. Cells were manufactured with wall thicknesses reduced by 35% and 45% with those of 35% performing equivalently to that of a standard cell. Cells with 45% reduced wall thickness have been manufactured and are going through testing at this point.

Automation advances were also made into application of the lanthanum chromite interconnection and lanthanum manganite cathode. The plasma spray unit was increased in capacity from spraying one part at a time to eight parts per cycle. This has reduced loading/unloading labor time as well as wear on the plasma spray unit with a reduced number of starts and stops on the gun arc. For cathode coating, the process has been changed from a dipping process to a localized spray process with an automated part indexing feature giving more uniformity to the coating. Figure 3 shows the comparison of a dipped to a sprayed cathode demonstrating the more open structure to allow for mass transport and provide triple phase sites. This uniformity and improved structure has lead to less variability in performance with cells achieving power on the higher end of the normal distribution curve.

Significant advances have also been made in generator design and geometry. In earlier designs, there were 126 cells required to generate 1.25 kW

Side view dipped cathode, x3.5k _

Side view sprayed cathode, x3.5k _

FIGURE 3. Morphology of a Dipped and Sprayed Cathode Tube

direct current. Under this project, that number has been reduced to 72, then 45, and presently 36 cells to achieve the same power level. This has also reduced stack weight by 75% from 92 to 23 lbs as well as volume by 82% from 44 L to <8 L. Gains have also been made in stack stability during thermal cycle as has been done on the individual cell. Figure 4 shows the stability of a standard cell stack under normal thermal cycle conditions. Cell stacks were reduced from the 800°C operating temperature to less than 200°C in less than one hour with subsequent heating back to 800°C in less than one hour. During twenty of these cycles, there was no noticeable decrease in performance from the stack. Also important from this test was the fact that the thermal cycles were done without the aid of a purge or cover gas on the anode side during cycle which would be required in any commercial product. During the last year, this same stack was subjected to testing with the fuel being steam reformed as opposed to the standard catalytic partial oxidation as used in the past. This

FIGURE 4. Stack Stability Testing

change in reformation technique as well as changes in the thermal distribution within the stack have resulted in efficiency gains from the mid 30's to the mid 40's for the same stack structure.

Conclusions and Future Directions

Significant strides have been made in achieving the goals set forth for stationary fuel cell generators under the DOE multi-year plan.

- Reduced cell thermal cycle degradation to <1%/100 thermal cycles from 20-30% to meet DOE stability and life objectives.
- Have reduced cell stack size by 82% and volume by over 75%.
- Have proven stack stability with purge less operation meeting needs of mCHP product requirement.
- Have achieved over 43% electrical efficiency (gross power/lower heating value natural gas) on latest stack technology.

Moving forward, the advances made in cell manufacturing will continue to achieve the desired DOE cost goals for stationary units through more automation and material reductions as well as yield improvements. Generator components will continue to be cost-reduced with further testing into life expectancy with the improved efficiencies demonstrated in the past year. The goal being to test a number of stacks with these conditions to generate sufficient data to determine repeatability and provide a platform to test cost reduction improvements.

FY 2009 Publications/Presentations

1. 2008 Fuel Cell Seminar, "Progress in Acumentrics' Fuel Cell Program", Phoenix, AZ, October 28, 2008.
2. 2009 DOE Hydrogen Program Review. Washington, D.C., May 20, 2009.

V.I.6 Renewable and Logistics Fuels for Fuel Cells at the Colorado School of Mines*

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Contract Number: DE-FG36-08GO8810

Subcontractors:

- Protonex Technology, LLC, Broomfield, CO
- Reaction Systems, LLC, Boulder, CO

Project Start Date: June 1, 2008
Project End Date: June 30, 2010

*Congressionally directed project

Objectives

- Develop solid oxide fuel cell (SOFC) materials for robust operation on diesel fuel.
- Identify optimal hydrocarbon-fuel reforming strategies.
- Create thermally stable fuel-reforming catalysts and supports.
- Employ system modeling to optimize auxiliary power unit (APU) configurations.
- Utilize model-predictive control to integrate system hardware.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) Durability
- (C) Performance

- (G) Start-up and Shut-down Time and Energy/Transient Operation

Technical Targets

In this project, we conduct a range of studies to improve the durability, efficiency, and transient operation of SOFC APUs. Insights gained from these studies will be applied toward the design and synthesis of SOFC materials and systems to meet the DOE 2015 technical targets for durability (35,000 hours), start-up time (15-30 minutes), and cycle capability (250 cycles).

Accomplishments

- Successfully fabricated next-generation, high-porosity, nickel-free, perovskite anodes from $(\text{La}_{0.75}\text{Sr}_{0.25})_{0.95}\text{Mn}_{0.5}\text{Cr}_{0.5}\text{O}_3$ (LSCM) materials, and applied initial deposits of yttria-stabilized zirconia (YSZ) electrolyte. The novel perovskite anode has far greater resistance to reoxidation and deposit-formation failure mechanisms than established nickel-YSZ SOFC anode materials.
- Demonstrated solid-state reaction sintering of barium-zirconate proton-conducting ceramics at $1/10^{\text{th}}$ the current fabrication cost.
- Demonstrated improved fuel-reforming strategies through selective oxidation of tar-forming species (such as ethylene).
- Synthesized novel thermally stable catalyst supports, and confirmed improved performance and stability at high-temperature (1,000°C) conditions.
- Designed, fabricated, and commissioned new catalyst test facility to examine catalyst operation on liquid fuel streams.
- Developed system modeling tools to examine 600-Watt SOFC APU generators utilizing low-sulfur diesel fuel.
- Established model-predictive control software, and demonstrated reduced-order models of high-fidelity physically based models for control of 600-W system.

Introduction

The objective of this project is to advance the current state of technology of SOFCs to improve performance when operating on renewable and logistics hydrocarbon fuel streams. While SOFCs can efficiently

convert the chemical energy of hydrocarbon fuels into electrical energy, the conversion process can prove problematic if not carefully controlled, due to the risk of carbon-deposit formation, sulfur contamination, and deviations from design set points. In this project, we will develop new SOFC and catalyst materials to improve the robustness of system operation on hydrocarbon fuel streams. Additionally, modeling and experimentation will be conducted to examine and mitigate the formation of carbon deposits during fuel-reforming and electrochemical-oxidation processes. Physically-based models will be developed to examine SOFC-system operation and performance in APU applications, including control strategies for improving the dynamic response of such SOFC APU systems. Finally, outreach will be conducted through creation of the Distinguished Lecturer Series to promote nationwide collaboration with fuel cell researchers and scientists.

Approach

The Colorado School of Mines (CSM) has assembled a strong and diverse team of scientists and researchers with broad skill sets applicable to fuel cell development. Coordinated through the Colorado Fuel Cell Center (CFCC), this team proposes to examine both the fundamental underpinnings and the key technical problems facing SOFC operation on renewable and logistics fuels. We will develop new SOFC materials and architectures for use with renewable and logistics (i.e. liquid hydrocarbon) fuel streams, addressing the technical challenges and operating windows associated with carbon-deposit formation and sulfur poisoning. We will develop catalyst materials and reforming strategies for optimal processing of liquid hydrocarbons and biomass-derived fuels for use in fuel cells.

We will develop system-integration strategies to create robust SOFC systems that utilize renewable and logistic fuels. Through advanced fuel cell modeling and simulation, we will examine the fundamental underpinnings of the atomic-scale charge-transfer processes occurring during SOFC operation on renewable and logistic fuels, incorporating the effects of load following and system control. Finally, we will promote outreach programs through the creation of a Distinguished Lecturer Series at the CSM campus to bring fuel cell scientists from across the nation in an exchange of ideas with faculty and students.

Results

Task 1: Ceramic Materials and Architecture

Fuel cell reliability and performance can be greatly improved through development of new materials and architectures that promote robust SOFC operation on renewable and logistics fuels. In this task, we investigate

new SOFC anode materials that promote tolerance to sulfur compounds and mitigate carbon-deposit formation. Additionally, we investigate alternative fuel cell architectures, seeking to optimize the structure of the cell for maximum efficiency and reliability. Computational modeling is combined with cell fabrication and testing to improve our understanding of the interdependence of cell materials, architecture, and performance.

We are developing a perovskite-based nickel-free anode material for achieving sulfur tolerance and robust, deposit-free operation on renewable and logistics fuels. The primary focus of our next-generation anode material is LSCM. LSCM is a mixed ionic-electronic conductor, and can provide both electronic and ionic conductivity in a single-phase perovskite material, making it ideal for use as an SOFC anode. Being a ceramic material, LSCM also shows greater resistance to carbon-deposit formation and sulfur poisoning in comparison to Ni-YSZ, but its catalytic performance and electronic conductivity is not well understood. In this task, we are examining the performance of LSCM over a wide range of environmental conditions, developing SOFCs that employ LSCM anode material, and evaluating the electrochemical performance of these cells under renewable and logistics fuel streams.

After developing preliminary materials formulations, we have begun coating LSCM anodes with thin (10- μm thick) YSZ electrolytes through a dip-coating process. A scanning electron microscope (SEM) image of a CFCC-fabricated LSCM-anode/YSZ-electrolyte assembly is shown in Figure 1. The micrograph in Figure 1a shows the YSZ surface of the tubular cell; the grain structure is clear, though some pinholes are evident. Improving the integrity of this electrolyte is the focus of our current efforts. The micrograph in Figure 1b shows a cross-section of the cell; the electrolyte has some measure of porosity, but is primarily dense. The LSCM fuel-side electrode shows an open morphology, as desired for facile gas transport. Current efforts are focused on improving the density of the electrolyte by creating a functionally graded electrode structure. We are now adding 10-micron-thick, fine-porosity, low-particle-size functional layers to the fuel-side electrode. These layers decrease the electrode porosity at the interface with the electrolyte, improve our ability to generate a dense electrolyte on a porous electrode, and increase the area of the triple-phase boundaries to increase power density. Such functional layers are common in Ni-YSZ cells, but have not been attempted with LSCM-based cells.

We have also developed a novel, inexpensive solid-state reactive-sintering (SSRS) technique for formation of $\text{BaZr}_{0.8}\text{Y}_{0.2}\text{O}_{3-\delta}$ (BZY20), a proton-conducting ceramic. The SSRS technique enables fabrication of near net-shape ceramic parts with density as high as 97% and

FIGURE 1. SEM of LSCM-based, tubular SOFC, a) YSZ-electrolyte surface; and b) fracture cross-section of LSCM anode-YSZ electrolyte assembly.

grain size as large as 5 μm while sintered at a relatively low temperature of 1,350°C. Now we are seeking to understand the fundamental formation and densification mechanisms for this process.

Task 2: Fuel Processing

Robust operation of fuel cells on renewable and logistic fuel streams hinges on the emergence of fuel-reforming technology that is compatible with SOFC requirements. In this task, we develop reforming strategies for optimal processing of liquid hydrocarbons as well as biomass-derived fuels for use in SOFCs. This task examines both external fuel reformers as well as on-anode reforming. The impact of gas-phase partial

FIGURE 2. Product Distributions as a Function of the DFM

oxidation reactions is explored as an alternative to tar and sulfur-mitigation strategies. This project involves three components: (1) identification of fuel surrogates, (2) characterization of relevant gas-phase kinetics, and (3) characterization of catalytic kinetics.

We have identified ethylene to be the gas-phase species that plays the most-critical role in the formation of deposits, and have explored potential routes for formation of ethylene during hydrocarbon reforming. For example, in the case of diesel autothermal reforming (ATR), one expects that the fuel might pyrolyze if it is not mixed with the steam/air oxidant stream. This has been confirmed in our ATR experiments. We have explored the impact of fuel mixing on the formation of deposit precursors. To simulate imperfect mixing or the degree of fuel mixing (DFM), we assumed a very simple model in which two separate reactors are used. One contains some fraction of the fuel with no steam or air (a pyrolysis reactor), while the remaining fuel fraction is perfectly mixed in the second reactor with all the steam and air (an oxidation reactor).

Figure 2 illustrates our results regarding how DFM affects the product distribution, assuming exothermic autothermal reforming conditions ($T_i = 800^\circ\text{C}$, $\text{H}_2\text{O}/\text{C} = 1.25$, $\text{O}/\text{C} = 1.4$, $\tau \sim 1$ s). Note in Figure 2 that ethylene (a deposit precursor) is formed in all cases of imperfect mixing. If only a part of the fuel mixed with the oxidant (e.g., DFM = 50%), this approach predicts formation of ethylene from the pyrolysis reactor and excess CO₂ production. The higher CO₂ level is directly traceable to the higher temperature predicted in the oxidation reactor. For the DFM = 50% case, the temperature of the oxidation part ($\sim 2,400$ K) is high enough to thermally damage the catalysts. Thus imperfect mixing is expected to result in an increased potential for both deposit formation and thermal damage to a catalyst. Furthermore, it is very interesting to note that the 100% mixing case has same product distribution to

equilibrium state, meaning that gas-phase reactions alone are sufficient to drive the system to equilibrium (no olefins or methane formed). We expect even more severe impact in diesel reforming since the large alkanes in diesel fuel are much more reactive than ethane. Therefore, enhanced mixing is essential to inhibit the formation of deposit precursors.

Also within this task, subcontractor Reaction Systems, LLC synthesizes thermally stable catalysts and catalyst supports and then measures their activity and stability for reforming of both renewable and logistics fuels. Novel catalyst supports have been fabricated, and the improvements in thermal stability demonstrated. Additionally, construction of a catalyst testing rig has been completed.

Reaction Systems characterized the thermal stability of the supports by measuring their surface areas after preparation and again after aging of the materials for eight hours at 1,000°C. This temperature reflects the upper end of those needed to obtain high concentrations of CO and H₂ during the catalytic partial oxidation reaction. We used the single-point Brunauer-Emmett-Teller method to measure surface area in all cases. The support surface areas before and after aging are listed in Table 1. Overall, the results indicate that aging at 1,000°C did not produce substantial reduction in these catalyst supports. Although the aging step needs to be increased in length, these results are encouraging because the sintering process, which causes surface area reduction, is most rapid in the initial stages of exposure to high temperature. Thus, we would expect even lower percent losses in surface area in subsequent periods of exposure.

TABLE 1. Support Surface Areas before and after Aging

Catalyst	Surface Area (m ² /g)		% Decrease
	As Prepared	Post Aging	
LaAl ₁₁ O ₁₈	56.3	56.7	< 0.1
SrAl ₁₁ O ₁₈	82.1	77.6	5.5
La-Al Mixed Metal Oxide (Fine Filter Paper Template)	20.7	19.2	7.2
La-Al Mixed Metal Oxide (Coarse Filter Paper Template)	13.5	14.1	<0.1

Task 3: System Optimization and Control

The system modeling and optimization effort centers on creating optimal SOFC-based APU system architectures, and is inclusive of an examination of dynamic component interactions during various

operating modes. Due to the importance of weight and volume constraints in mobile applications, opportunities for process intensification through the quantitative evaluation of novel reactive heat exchanger hardware within the system will be examined. Modeling and analysis efforts shall be applied to the ongoing APU development efforts of Protonex Technology Corporation with the specific aims of improving both system performance prediction under sensor uncertainty and heat-loss estimation methods.

A preliminary energy and exergy analysis on a 600-W Protonex SOFC system was completed in order to understand the energy flows and to pinpoint thermodynamic inefficiencies in the design. The utility of this type of analysis is both in locating and quantifying the magnitude of the irreversible losses and identifying opportunities to improve the system efficiency. Figure 3 depicts the finalized energy and exergy flow diagram for the baseline Protonex APU system. The system components are not adiabatic devices, and this is reflected in the flow diagram which depicts both component thermal energy and exergy flows that are rejected from the component to the hot-zone surroundings.

Overall, 3.0 kW of energy (2.98 kW exergy) associated with the liquid hydrocarbon fuel flows into the system. Exergetic analysis in reforming of the fuel indicates that the process occurs at an exergetic efficiency of approximately 80%. Some 490 W of exergy are destroyed within the catalytic partial oxidation (CPOx) unit itself and an additional 120 W are lost via heat transfer to the hot zone surroundings. By comparison, the SOFC tube bundle operates at an exergetic efficiency of 84.3%, slightly higher than the CPOx unit, and most of the irreversibility occurs within the unit.

The tail-gas burner and the recuperative heat exchanger operate with exergetic efficiencies of 71.8% and 44.6%, respectively. Heat loss from the hot-zone surface to the surroundings is over 700 W, and the hot system exhaust carries away an additional 1.66 kW of thermal energy (0.65 kW exergy). Overall, the system exergetic efficiency is 20.1%, and opportunities for improvement appear to reside with improving the thermal management within the hot zone of the system and reducing the hot exhaust gas temperature. Improvements via process intensification might include integration of a tail-gas burner and recuperator to reduce these inefficiencies. Such system modifications will be investigated as the project moves forward.

The goal of the Fuel Cell System Control task is the design of a control system to regulate the operation of a complete SOFC system. The control system design is based on a dynamic model that can predict system behavior given perturbations in actuator settings, such as air and fuel flows and power loads. Ideally, these models are based on physical first principles; however,

FIGURE 3. Energy/Exergy Flow Diagram of 600-W Protonex APU System

physically-based models are often very complex, and take considerable computational resources to compute. When utilized for real-time control, computational complexity can become a limiting factor in the usefulness of the model, and it becomes necessary to capture the dominant behavior in a lower order model that can be run quickly. Our approach is to start with physically-based models, and apply system-identification techniques to develop the required reduced-order models.

Eventually, this project will encompass the entire fuel cell system, but current work has focused on control of the fuel cell stack in isolation. The control strategy for the fuel cell stack is illustrated in Figure 4. We have implemented this reduced order model in MATLAB/Simulink, along with the state estimation and model-predictive control components. The state-estimation component uses the reduced-order model of the plant and measurements of the inputs and outputs to find the current internal state that best matches the observed behavior. Then, the model-predictive-control component calculates the future actuator commands that are needed to drive the system from the current state to the desired future behavior. This future behavior is specified in terms

FIGURE 4. Control Strategy for the Fuel Cell Stack

of either desired signal trajectories (e.g. current set-point) or desired signal bounds (e.g. minimum voltage or fuel utilization). The current implementation of the model-predictive control is a strategy based on online optimization, but we will be working in the future to develop a pre-computed implementation based on recent work in multi-parametric optimization.

An example of feedback control is shown in Figure 5. In this figure, the controller adjusts the cell voltage and fuel flow rate to meet a desired current output trajectory while at the same time meeting

FIGURE 5. Example of current control while meeting constraints inputs and outputs. Blue lines represent constraints.

constraints on the inputs and outputs, which are shown as horizontal blue lines. In particular, note that the current trajectory is achieved while meeting the lower constraint on hydrogen mole fraction in the exhaust.

Task 4: Outreach

In this task, CSM hosts a seminar series that brings prominent fuel cell researchers to the CSM campus for interaction with our students and our faculty. This exchange of ideas will promote national collaboration, further the development of fuel cells, and grow the CSM program. During the previous year, many speakers have participated in the program. Dr. Ellen B. Stechel of Sandia National Laboratories provided CSM students and faculty with a talk entitled “Sunshine to Petrol,” reviewing Sandia’s program on conversion of solar power to liquid-hydrocarbon fuels. Additionally, scientists Annamalai Karthikeyan (Harvard University) and Jianhua Tong (California Institute of Technology) visited the Colorado School of Mines and provided overviews of their research in well-attended seminars. One visit led to an offer of employment for Dr. Tong, who is now a research professor in the Metallurgical and Materials Engineering Department at CSM, and works actively on materials development for this DOE project.

Future Directions

Task 1: Ceramic Materials and Architecture

- Measure electrical conductivity and catalytic activity of novel anode compositions over a range of anode conditions.

- Measure the ionic conductivity of protonic conductors.
- Evaluate the long-term stability of protonic conductors using thermal gravimetric analysis, differential thermal analysis, and dilatometry.

Task 2: Fuel Processing

- Extend gas-phase mechanism to characterize selective partial oxidation of tars.
- Extend partial-oxidation experiments to toluene.
- Develop process windows for deposit-free SOFC operation.
- Measure catalyst activity and stability for logistics-fuel reforming.
- Conduct extended-aging tests with catalysts and support materials.

Task 3: System Optimization and Control

- Create optimal system configurations for liquid-fueled SOFCs.
- Including anode recycle with ATR.
- Evaluate performance/cost advantage of process-intensification efforts.
- Extend reduced-order model to complete SOFC system, including CPOx.
- Experimentally validate models: CPOx-control experimentation under development at CSM; collaborate with industrial partner and subcontractor (Protonex) for experimental data.

- Implement explicit form for Model Predictive Control.
- Drastically reduce requirements for computational control.

FY 2009 Publications/Presentations

1. J. Tong, D. Clark, M. Hoban, R. O'Hayre, "Cost-effective solid reaction method for proton conducting yttrium-doped barium zirconate ceramics," 17th International Conference on Solid State Ionics, Toronto, Canada, June 28, 2009.
2. M. Sanders, S. Elangovan, G. Coors, R. O'Hayre, "Results of steam flux measurements in BZY20," 17th International Conference on Solid State Ionics, Toronto, Canada, June 28, 2009.
3. M. Sanders, S. Elangovan, G. Coors, R. O'Hayre, "Using dilatometry to measure the hydration thermodynamics of perovskite-based steam-permeable ceramics," 8th International Pacific Rim Conference on Ceramics and Glass, Vancouver, B.C., June 1–5, 2009.
4. M. Sanders, G. Coors, R. O'Hayre, "Modeling of material parameters for increased steam permeation in gadolinium-doped barium cerate ceramic membranes," 6th Annual ASME Fuel Cell Science and Technology Conference, Denver, Colorado, June 17th, 2008.
5. I. Kang, A.S. Al Shoaibi, H.-H. Carstensen, and A.M. Dean, "Ethylene pyrolysis and the subsequent molecular weight growth reactions," American Chemical Society National Meeting, March 22–26, 2009.
6. L. Huynh, A.S. Al Shoaibi, H.-H. Carstensen, and A.M. Dean, "Low-temperature partial oxidation of ethane and propane," American Chemical Society National Meeting, March 22–26, 2009.
7. D. Storjohann, J. Daggett, N.P. Sullivan, R.J. Kee, H. Zhu, S. Menzer, D. Beeaff, "Fabrication and evaluation of SOFC anodes employing reaction-sintered yttria-stabilized zirconia," Journal of Power Sources, accepted for publication, 2009.
8. J. Daggett, N. Sullivan, R. J. Kee, H. Zhu, A. Dean, "Ethanol transport and chemistry in solid-oxide fuel cells," 6th Annual Fuel Cell Science, Engineering & Technology Conference, Denver, CO, June 16–18, 2008.
9. D. Storjohann, S. Menzer, D. Beaff, J. Daggett, R. Kee, N. Sullivan, "Comparative study of reaction-sintered anode-supported tubular solid oxide fuel cells," 6th Annual Fuel Cell Science, Engineering & Technology Conference, Denver, CO, June 16–18, 2008.

V.I.7 Low-Cost Co-Production of Hydrogen and Electricity*

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Contract Number: DE-FC36-0515195

Subcontractors:

- University of Alaska, Fairbanks, AK
- Udelhoven Oilfield System Services, Anchorage, AK

Vendors:

- H2 Pump LLC, Latham, NY
- Giner Electrochemical Systems LLC, Newton, MA

Project Start Date: November 13, 2006

Project End Date: December 31, 2009

*Congressionally directed project

Objectives

- Demonstrate efficient, reliable and durable solid oxide fuel cells for stationary applications.
- Demonstrate co-production of electricity and hydrogen.
- Determine the feasibility of a delivered cost of hydrogen below \$2.50 per gge by 2010.

Technical Barriers

From the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan, specific technical barriers addressed by this project are:

Section 3.4: Fuel Cells

- (A) Durability
- (B) Cost
- (C) Performance

Section 3.6: Technology Validation

(I) Hydrogen and Electricity Co-Production

Technical Targets

TABLE 1. Progress towards Meeting Technical Targets for Low-Cost Co-Production of Hydrogen and Electricity

Characteristic	Target	Current Status
PSOFC Performance (System efficiency)	>45% PSOFC system efficiency $\eta = (\text{AC power exported to grid}) / (\text{LHV natural gas})$	Achieved >45% PSOFC system efficiency on both systems in Alaska; 51.1% peak system efficiency
PSOFC Performance (Peak grid-tied power)	25 kW grid-tied fueled by natural gas	> 25 kW grid-tied demonstrated on both systems in Alaska; 25.9 kW peak
PSOFC Performance (Durability)	Operate system for 1 year in the field	Both systems operating since December 3, 2008; each has >5,000 h runtime with >97% availability at > 15 kW grid-tied (as of June 30, 2009)
Hydrogen Purity	Sufficient purity to power a PEM fuel cell	Demonstrated hydrogen purity with undetectable levels of CO and CO ₂ (<1 ppm) and -70°C dewpoint using enhanced hydrogen pump
Hydrogen Production	19 kg/day peak hydrogen production by purifying PSOFC anode exhaust	Full-scale hydrogen pump purified simulated PSOFC exhaust at flow rates up to 19.3 kg/day; Integration testing with PSOFC system has commenced
Distributed production of hydrogen from natural gas	2010 Target: \$2.50/gge (delivered)	DOE H2A model estimates \$4.53/gge without taking any credit for electricity produced; Estimate drops to \$0.97/gge with \$0.12/kWh credit for electricity

PSOFC – planar solid oxide fuel cell; AC – alternating current; LHV – lower heating value; PEM – proton exchange membrane; gge – gasoline gallon equivalent

Accomplishments

- Demonstrated rated power of 25 kW grid-tied for both PSOFC systems in Alaska fueled by natural gas using standard Bloom Energy hot boxes.
 - Project was planned for field demonstration of a single 25 kW system.

- All balance-of-plant components have been validated on two operational systems in Alaska; each has >5,000 h runtime with >97% availability at >15 kW grid-tied, as of June 30, 2009.
- Demonstrated 51.1% PSOFC peak system efficiency (η).
 - $\eta = (\text{AC power exported to grid})/(\text{LHV natural gas})$.
- System remotely monitored 24-7 by team of trained operators.
- Full-scale hydrogen pump purified simulated PSOFC exhaust at flow rates up to 19.3 kg/day.
 - Integration testing with PSOFC system has commenced.
- DOE H2A model used to estimate cost of co-producing hydrogen at below \$2.50/gge when taking credit for value of electricity produced.
 - Estimate drops below \$1/gge with \$0.12/kWh credit for electricity.

Introduction

Bloom Energy's fuel cell systems, when manufactured in high volume, can produce low-cost hydrogen by co-producing hydrogen and electricity simultaneously with one common set of low-cost equipment. The main objectives of this project are to 1) deliver and field test a fuel cell electricity generator in Alaska; 2) demonstrate hydrogen production from a hydrogen pump in a lab-based fuel cell system similar to that to be operated in Alaska; and 3) analyze the feasibility of a delivered cost of hydrogen below \$2.50 per gge.

Approach

The project is divided into two phases. Phase 1 includes the build of a PSOFC electricity generator; the design, permitting and build of a demonstration site; and the installation, commissioning and start up of the generator. This phase also includes evaluation of several hydrogen production technologies for integration and validation with a lab-based PSOFC.

Phase 2 covers the one-year demonstration of the PSOFC electricity generator. It also includes the build, test and demonstration of the hydrogen generation sub-system. The delivered cost of hydrogen, using the DOE H2A model, is also included in Phase 2. More specifically, the following is included:

- Test a vendor-provided hydrogen pump prototype in stand alone mode (completed).

- Analyze the volume and purity of hydrogen produced by prototype unit (completed).
- Design the integration of the vendor-provided hydrogen pump production unit with our PSOFC system (completed).
- In our lab, test the hydrogen pump integrated with our PSOFC system (in process).
- Analyze the volume and purity of hydrogen produced (in process).
- Operate the PSOFC system in the field for 12 months (in process).
- Analyze the efficiency and availability of the fuel cell (in process).
- Analyze the results of PSOFC electricity and hydrogen co-production (pending).

Results

Phase 1 of the project is complete. Phase 2 is in process. The PSOFC demonstration began in November 2008 and demonstration readiness of the H2 Pump hydrogen production system began in 2008.

Fuel Cell Demonstration

The fuel cell demonstration site in Anchorage, Alaska was designed and permitted in the first quarter of 2008. Construction completion and operational permitting occurred in October 2008. Two 25 kW PSOFC modules were installed, commissioned and started up in November 2008. Approval to grid connect was received on December 1, 2008. The one-year demonstration started on December 3, 2008. System demonstration objectives are projected as follows:

- 25 kW peak grid-tied power
- Operation on natural gas
- Operate at 480 V
- Grid parallel operation
- Remote monitoring
- 70% uptime over one year demonstration
- 45% peak net electric efficiency in electric-only mode

As of June 30, 2009, system performance is listed in Tables 2 and 3.

TABLE 2. System 1C Performance Statistics December 3, 2008 – June 30, 2009

25 kW Operation	System 1C	
Average AC Efficiency	44	%
Peak AC Efficiency	51.1	%
Total Energy Output	100,182	kWhrs
Total Fuel Consumption	22,771,244	L
Peak AC Power	25.9	kW
Hrs On-Site	5,023	hrs
Uptime	5,002	hrs
Load Hrs	4,895	hrs
Availability at 15.0 kW+	97.3	%
Grid Faults	9	
System Faults	10	

TABLE 3. System 1D Performance Statistics December 3, 2008 – June 30, 2009

25 kW Operation	System 1D	
Average AC Efficiency	45	%
Peak AC Efficiency	49.1	%
Total Energy Output	103,267	kWhrs
Total Fuel Consumption	22,902,074	L
Peak AC Power	25.4	kW
Hrs On-Site	5,023	hrs
Uptime	5,010	hrs
Load Hrs	4,897	hrs
Availability at 15.0 kW+	97.5	%
Grid Faults	7	
System Faults	4	

Hydrogen Production Demonstration

A hydrogen pump from H2 Pump, LLC of Latham, New York was chosen as the demonstration vehicle for the hydrogen production portion of the project. A small-scale H2 Pump product was validated at Bloom Energy's laboratories and demonstrated that hydrogen pumping: 1) is scalable, 2) has high electrochemical efficiency (low power required/kg H₂), 3) is a continuous flow device having a near infinite turn down ratio with minimal parasitics when not pumping hydrogen, and 4) can pump hydrogen on demand. A 120-cell H2 Pump was procured and the design for integration to a 25 kW PSOFc was completed.

Hydrogen production will be demonstrated in the next reporting period. Objectives are as follows:

- Two operational modes
 - Hydrogen recycle
 - External hydrogen delivery
- SOFC operation at 95% fuel utilization in recycle mode
- 2,000 hours test duration, with <5% performance degradation of hydrogen production.

In addition to the hydrogen pump, a partial pressure swing adsorption (PPSA) prototype was specified and contracted for development. Delivery is expected in September 2009. It is expected that the PPSA will be operated as follows:

- No water-gas shift required
- Low parasitic electrical power
- Anode exhaust to be separated
 - Flow rate: 99 slpm
 - Temperature: 30°C
 - Supply pressure: 5 inches water column
 - H₂ (29.3%), CO₂ (66%), H₂O (3.4%) and CO (1.3%)
- PPSA effectiveness
 - 80% fuel recovery (CO, CH₄, H₂)
 - 95% CO₂ separation

Hydrogen Cost Analysis

The DOE H2A cost model was used to estimate the cost of co-producing hydrogen from a distributed PSOFc system without taking credit for the value of electricity produced. For the assumptions stated in the Current Analysis (H2A Model) shown in the right column of Table 4, the DOE H2A model estimates the delivered cost of hydrogen to be \$4.53/gge without taking any credit for the value of electricity produced. This is very close to the \$4.82/gge estimated by scaling the modeling performed at Bloom Energy (BE) when this project was proposed in 2005 to a 200 kW output and increasing the capacity factor from 90% to 98%.

By taking credit for the value of electricity produced, the estimated delivered cost of hydrogen drops considerably and can be below \$1/gge. Using the DOE H2A model and assuming \$0.12/kWh for the value of electricity, the delivered cost of hydrogen is \$0.97/gge, as shown in Table 5.

TABLE 4. Hydrogen Cost Analysis Using the DOE H2A Model

H₂ Cost Analysis Using DOE H2A Model		
	Original Proposal (BE model)	Current Analysis (H2A Model)
Installed Capital Cost	\$1,500/kW	\$1,500/kW
Overall System Efficiency	56%	56%
Overall Electrical Efficiency	33%	33%
Natural Gas Cost	\$8/mmBtu	AEO 2007
Capacity Factor	90%	98%
H ₂ /Year	50,192 kg	54,656 kg
Electrical Output	200 kW	200 kW
Delivered cost of H ₂ /gge	\$4.82	\$4.53

BE & H2A models are very consistent; differences are in assumed capacity factor

TABLE 5. Hydrogen Cost Analysis Adding the Value of Electricity

H₂ Cost Analysis Adding Value of Electricity		
	Original Proposal (BE model)	Current Analysis (H2A Model)
Delivered cost of H ₂ /gge	\$4.82	\$4.53
Value of Electricity	\$0.12/kWh	\$0.12/kWh
Electrical output	1,576,800 kWh/year	1,716,960 kWh/year
Value of annual output	(\$167,360)	(\$182,240)
H ₂ /Year	50,192 kg	54,656 kg
Value of Electricity/kg H ₂	(\$3.77)	(\$3.77)
H ₂ cost, net/gge @ 300 psi	\$1.26	\$0.97

Projections are consistent with DOE delivered cost of H₂ goals

Conclusions and Future Directions

Next steps in this project include the following:

- Complete PSOFC system demonstration in Anchorage, Alaska.
- Complete H2 Pump demonstration.
- Validate PPSA design.

FY 2009 Publications/Presentations

1. A presentation was made at the DOE Hydrogen Program Annual Merit Review held in Crystal City, Virginia in May 2009.

V.I.8 Development of a Novel Efficient Solid-Oxide Hybrid for Co-Generation of Hydrogen and Electricity Using Nearby Resources for Local Application*

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Contract Number: DE-FG36-05GO15194

Subcontractors:

- University of Alaska Fairbanks, Fairbanks, AK
- Missouri University of Science and Technology, Rolla, MO
- University of Utah, Salt Lake City, UT

Project Start Date: February 10, 2006
Project End Date: July 31, 2009

*Congressionally directed project

Objectives

- Develop and optimize composite cathodes for solid oxide fuel-assisted electrolysis cells (SOFECS).
- Fabricate anode-supported solid oxide fuel cells (SOFCs) and SOFECS with Ni + yttria-stabilized zirconia (YSZ) anode supports, thin-film YSZ electrolytes, and composite cathodes.
- Quantify the issues affecting the mechanical stability (particularly the strength) of the anode supports, followed by characterization of the anodes.
- Develop glass seals.
- Demonstrate SOFEC-SOFC hybrids co-generating hydrogen and electricity directly using hydrocarbon fuels at 800°C.
- Design, construct, and evaluate a 5 kW module-based SOFEC-SOFC system for co-generation of hydrogen and electricity directly using natural gas.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Generation by Water Electrolysis section (3.1.4.2.2) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (G) Capital Cost
- (H) System Efficiency

Technical Targets

This project is conducting the research and development of an advanced technology that cogenerates hydrogen and electricity directly using the distributed natural gas based on a hybrid SOFEC-SOFC. Insights gained from this project will be applied toward the future design and construction of hydrogen and/or electricity cogeneration systems that meet the following DOE 2012 distributed hydrogen production targets:

- Hydrogen cost: \$3.7/gallon of gasoline equivalent (gge)
- Energy efficiency: 69% (lower heating value)

Accomplishments

- Completed the design of a stand-alone 5 kW co-generation system.
- Defined specifications and purchased off-the-shelf hardware for the hybrid system.
- Fabricated and pre-tested major balance-of-plant (BOP) components.
- Developed an interconnect brazing system featuring significant cost-savings in materials and machining.
- Completed fabrication of anode-supported cells necessary for module-based 5 kW hybrid stacks.
- Completed fabrication of non-cell repeat stack units.
- Conducted and demonstrated long-term stability tests of SOFEC stacks operation for up to 360 hours, no significant degradation was observed.
- Constructed and evaluated a kW SOFC stack with refined manifold designs featuring thermal and fluid flow management enhancements.
- Assembly and burn-in cycle tests of SOFEC-SOFC hybrid modules are underway.

Introduction

Developing safe, reliable, cost-effective, and efficient hydrogen-electricity co-generation systems is an important step in the quest for national energy security and minimized reliance on foreign oil. This project focuses on materials research and development of a novel planar solid-oxide hybrid for hydrogen and electricity co-generation directly using fuels such as distributed natural gas and/or coal-derived fuels. The innovative hybrid system under development uses reversible SOFECs integrated with SOFCs, both of which are anode-supported solid oxide electrochemical cells. The SOFECs and SOFCs are manifolded in a stack such that the anodes of both the SOFECs and the SOFCs are fed the same fuel, such as natural gas or syngas. Hydrogen is produced by SOFECs and electricity is generated by SOFCs within the same hybrid system.

Redox stable cathodes for the reversible SOFECs have been developed, using composite cathodes comprising p-type and n-type materials. The performance of each composite has been carefully evaluated as a cathode and suitable materials have been selected and optimized. Although the main factors influencing the design are electro-chemical in nature, the requirement to operate the components at elevated temperatures and the need for thermal cycling between room and operation temperature has made thermomechanical aspects of the components extremely important. In order to achieve the high power densities possible for SOFEC-SOFC hybrid stacks, reliable hermetic sealing technologies have been developed. Hydrogen and electricity cogeneration concept has been proofed at a 1 kW stack level, but questions about complexity of hybrid stacks integration and concept demonstration at a system level make the development of a complete hybrid system a priority.

Approach

This project is to develop and demonstrate a 5 kW hybrid system based on advanced solid-oxide electrochemical cells to cogenerate hydrogen and electricity directly using natural gas, coal-derived syngas, and other type of fuels. The research and development efforts have been conducted by a team led by Materials and Systems Research, Inc. (MSRI), including University of Alaska Fairbanks, Missouri University of Science and Technology, and University of Utah.

In order to achieve the project objectives, project efforts have been shifted from focusing on electrodes and sealing materials research and development, to developing SOFEC-SOFC hybrid stacks and dedicated SOFC stacks design and fabrication, to proof-of-concept demonstration of cogeneration at cell and

stack levels, and finally to system design, manufacture and experimental verification. Perovskite-type (La,Sr)(Cr,Mn)O₃-based composite cathodes have been developed and the materials' redox stability has been demonstrated in both reducing and oxidizing atmospheres. Elastic properties, as well as equibiaxial flexural strength of Ni+YSZ-based anode substrates were evaluated in both air and reducing environments simulating the actual operating conditions of the SOFEC-SOFC hybrid stacks. The influence of glass particle sizes on glass-ceramic crystallization behavior was characterized using a hot-stage microscopic technique. SOFECs and stacks were fabricated and long-term stability tests of the stacks were performed for hydrogen production. Once the proof-of-concept of cogeneration was demonstrated at a stack level and sufficient know-how and understanding had been obtained, the research efforts were carried to the development and demonstration of hydrogen and electricity cogeneration at a system level. A stand-alone 5 kW system comprising module-based SOFEC-SOFC hybrid and dedicated SOFC stacks, BOP components, and electronic controls was designed. Major BOP components have been fabricated and off-the-shelf hardware was purchased, followed by evaluation under the forecasted operating conditions. Meanwhile, the system design will be refined and assembled for final evaluation.

Results

Stack Design and Fabrication: In the past year, a great amount of efforts has been made to complete design and fabrication of anode-supported solid oxide electrochemical-cells and stacks necessary for a 5 kW system. This 5 kW system consists of six modular stacks, including three hybrid SOFEC-SOFC stacks with hexagonal design for hydrogen and power coproduction, and three dedicated SOFC stacks with square design for power generation. Figure 1 is a picture of the completed 360 cells to be assembled into six modules. Stack manifolds were designed and refined for providing a unique flow pattern such that both gas flow and temperature distributions are uniform, leading to minimized stack pressure drop and enhanced thermal management. A process to braze interconnect was developed in-house by acquiring and engineering a spray system to precisely control the uniformity of coating layers with optimum thickness. With this process, high yield and high quality interconnect assemblies were fabricated without creep-flattening at a significant cost-saving in materials and machining. The electronic resistance of brazed interconnect assembly was low, even after extended operation at 800°C.

Stack Evaluation: The initial conditioning and testing of each stack module will be conducted in a separate test station before being assembled into the 5 kW hybrid system. Figure 2 shows the performance

FIGURE 1. Picture of 360 Cells to be Assembled into Six Modules

characteristics of a forty-cell stack operated in the SOFC mode for power generation. At 800°C and fixed utilizations of 40% for both fuel and air, the stack generated 930 watts of electric power at 30.4 A. The average per-cell voltage was 0.764 V. The background of Figure 2 is a picture of the stack post-test, with the stack dimension of 6"x6"x5".

5 kW Hybrid System Development: The hybrid system design and component integration for cogenerating hydrogen and electricity directly using natural gas is preceded by solid modeling of the various BOP components and creation of an assembly of these component models. In the past year, the system design has undergone several revisions in order to reduce the system cost and improve the flexibility of the control system. The final system will be constructed with assembly of a hot-zone comprising six modular stacks, a BOP components zone, and an electronic control zone. Figure 3 is a rendering of the system configuration showing the major sub-systems, inlet and outlet streams. In the hot-zone, a spring-plate compression device will be used for each individual stack with insulated tension rods and load plates that allows the springs to remain relatively cool while minimizing thermal losses from the stack enclosure. Six pairs of the compression devices were manufactured. The individual stack modules will then be assembled to an electrically insulating support plate that separates the stack hot-zone enclosure from the BOP components. Gas feed pipes, welded to each manifold/compression plate, will pass through the support plate and be sealed in compression fittings to the BOP piping. If it is necessary to remove an individual stack for maintenance or replacement, this can be done without removing the compression force from the other stack modules. The major hot BOP components, including the tailgas-fired combustors and reformers, were designed and manufactured with improved catalytic combustion features for stable flame and heat transfer enhancement. Additional features were also

FIGURE 2. Performance Characteristics of a kW Stack Tested in SOFC Mode

FIGURE 3. Rendering of the 5 kW Hybrid System Configuration

considered for allowing for disassembly and replacement of individual BOP components, as well as access to the catalyst beds. Compact heat exchangers were purchased for recuperating heat from cathode gases to combustion air. A central tailgas-fired boiler supplies steam to the reformers and SOFC cathodes with separate control mechanisms. The boiler with a shell-and-tube configuration loaded with catalyst on diffuser screens was constructed and tested for providing 130 standard liters of steam per minute under steady state operation. The commercially available multi-module C-DAQ hardware was purchased to build the control system with a user interface operating National Instrument's LabView software.

Conclusions and Future Directions

A significant amount of effort have been made at MSRI to research and develop the advanced technology that cogenerates hydrogen and electricity directly

using chemical energy of fuels to replace the electricity necessary for conventional water/steam electrolysis. MSRI has developed redox stable electrodes and demonstrated stability for more than 5,000 hours. MSRI also developed state-of-the-art planar, SOFEC-SOFC hybrid stack technology, and demonstrated the best and highest performance reported yet at 1 kW stack level.

- Extensive experimental studies conducted at MSRI show that hydrogen production using the advanced SOFEC technology is a viable pathway to reduce the cost of hydrogen.
- Long-term tests of SOFECs at both single-cell level and stack level proved that materials developed at MSRI are applicable to the reversible SOFECs/SOFCs.
- Strong collaboration between the industry and academia encouraged material research and development.

- Test of the 1 kW SOFC stack showed the features of newly designed stack architecture of thermal and fluid flow management enhancement.
- Modular characteristics of SOFEC-SOFC hybrid impart a great flexibility to a system design for hydrogen production that fits various needs.

For the remainder of the project, a hybrid system will be constructed and tested to demonstrate co-generation of hydrogen and electricity directly using natural gas. Cost analysis of hydrogen production using the hybrid SOFEC-SOFC technology will be performed for future system optimization. Important technical findings and results will be prepared for journal publication and conference presentations.

V.I.9 Biogas-Fueled Solid Oxide Fuel Cell Stack*

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Contract Number: DE-FG36-08GO88109

Project Start Date: July 1, 2008

Project End Date: December 15, 2009

*Congressionally directed project

Objectives

The objective of this project is to develop and demonstrate a 400 Watt solid oxide fuel cell (SOFC) stack and evaluate its performance on hydrogen and biogas:

- Cost-effective SOFC manufacturing.
- Electric power generation from different biogas compositions.
- 400 Watt stack design and build.
- Demonstrate 400 W of power output on hydrogen and biogas.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) Durability
- (B) Cost
- (C) Performance

Technical Targets

This project focuses on maximizing the production efficiency, while at the same time increasing the reliability and reproducibility of the SOFCs. The focus of development efforts will be to optimize the catalytic

materials and operating conditions that will be utilized in the construction and evaluation of a 400 W_e stack with a power density of 0.35 W/cm².

- Fabricate 150 single cells with a minimum power of 10 Watts and a power density of 0.35 W/cm² on hydrogen at 800°C.
- Optimize the fabrication process to achieve a cell production yield of at least 70%.
- Optimize cell operating conditions for biogas (fuel flow rate, feed gas composition, temperature) to achieve maximum power.
- 200-thermal cycling test on single cell.
- 500-hour endurance test on single cell using biogas.
- 400 W stack design that will allow for modular integration in to kilowatt-class applications.
- 400 Watt stack test with hydrogen and biogas at varied compositions.

Accomplishments

- Achieved cell fabrication yields above 60% associated with a 50% reduction in cell cost and 58% reduction in processing time.
- Cell materials have been optimized for obtaining desired microstructure and composition yielding higher power output.
- Achieved >525 mW_e/cm² producing >9.5 W_e on biogas.
- Operated the cell for >200 thermal cycles.
- Achieved stable power output for >500 hours on biogas.
- Designed a single module stack that has been successfully tested on biogas.

Introduction

Increased demand for fossil fuels is imposing massive impact on the environment and also leading to unprecedented fuel prices. Efficient power conversion technologies that utilize secure renewable energy are urgently needed. High-efficiency clean energy technologies such as SOFCs have shown great potential to reduce carbon emissions, reduce the nation's dependence on petroleum-based fuels, and utilize a wide range of fuel resources including biomass gas.

The scope of this project is to develop and demonstrate a 400 Watt stack using advanced SOFC technologies. The stack will employ single fuel cells manufactured by a cost-effective manufacturing

approach that is suitable for scaling to larger systems. In addition to hydrogen fuel, the stack will be operated on biogas.

Approach

To achieve the project objectives, novel cell fabrication route will be implemented and optimized for materials and cell microstructure. This new fabrication process will enable quick turnover of the cells with reliable and efficient performance in addition to reduced costs associated with both materials and labor.

The cells are designed to: (1) operate on both hydrogen and biogas (methane + carbon dioxide) with an integrated catalytic layer to perform fuel processing; (2) withstand >200 thermal cycles from 200-800°C; and (3) provide stable performance for >500 hours on biogas fuel. All these properties will be enabled by a careful selection and consideration of conductivity, chemical stability, thermal expansion coefficient mismatch, physical stability, and activity of the fuel cell materials.

A 400 W stack will be designed, constructed and tested utilizing the cells produced by the above process. The stack feasibility test will involve power generation via hydrogen and biogas at different compositions.

Results

One of the prime objectives was to achieve high power densities at higher power output. The fabrication process was optimized to obtain the desired microstructure by considering the material combinations, process conditions, physical and chemical stability, thermal and electrical conductivity, and thermal expansion coefficient of the materials. Optimization of the SOFC materials resulted in improved power output, manufacturing yield, and decreased processing time. Processing times have been decreased by 58% compared to the extrusion process.

Figure 1 shows a comparison of gravimetric and volumetric power densities of different cell technologies. The cells made with the new fabrication process and optimized material set outperformed the ones that were made with conventional process, demonstrating a three-fold increase in the performance by packing more power per unit mass, volume and specific surface area. These higher power densities were made possible by optimizing the anode and cathode materials/process to obtain a porous structure for lowering the mass transfer resistance.

In addition, these cells demonstrated very high electric efficiency (electric power produced vs. fuel's energy value) and fuel utilization because of the enhanced microstructure. Experiments were conducted to find out the effect of fuel flow rate on the power output and efficiency of the cell. The cells utilized in

FIGURE 1. Power Density Comparison of Different Cell Technologies

the previous phase of this project showed a significant decrease in power output at lower flow rates. However, the newer SOFCs utilized under the current project showed relatively little decrease in power in spite of 40% drop in the fuel supplied. This translates to a higher overall efficiency, as shown in Figure 2, the cell power reaches as high as 9 watts at 50% electric efficiency and 12 Watts at 37% efficiency. These cells also showed very high performance even at lower operating temperatures, where the cell produced 83% of the peak power at 700°C compared to its peak operating temperature of 800°C.

One of the major considerations in utilizing biogas for an SOFC system is its composition, which depends entirely upon the raw material fed into the decomposition unit processors, such that the fuel composition would be unique to each processing facility. In order to develop a biogas-fed SOFC, the cells must have a high performance over a wide range of biogas compositions. An experiment was hence conducted by feeding biogas containing same energy value (lower heating value of methane) with different concentrations viz. 60%, 50% and 40% of methane and a balance of carbon dioxide resulting in rich, equimolar and poor quality feed streams that is typical of different waste treatment plants. The power output varied by ~5.5% as the gas quality changed from rich to poor quality. This is a direct result of the oxidant concentration in the feed stream which in turn affects the amount of electrochemically oxidizable species.

Similar to the hydrogen performance, the cell's efficiency to convert the available energy of biogas in to electricity increased at lower flow rates, reaching up to 40% while producing >8 Watts of electric power (Figure 3). It has to be noted that the tests were performed by flowing the feed through an SOFC in a single pass. This efficiency can be further improved on a stack scale by recycling some of the exhaust. For a

FIGURE 2. Effect of Fuel Flow Rate on Power Output and Efficiency of the Modified SOFC

FIGURE 4. Estimated Power Output from the SOFC Stack as a Function of Operating Temperature on Biogas Fuel

FIGURE 3. Effect of Rich-Quality Biogas Flow Rate on Power Output and Electric Efficiency of a SOFC Operated at 800°C

portable system, efficiencies above 40% are considered to be a significant achievement.

All of the above results show excellent performance of the SOFC at wide range of operating conditions producing 8-12 Watts of electric power depending on the fuel type and flow rate. It is important that these cells demonstrate stable performance with time especially under the conditions of direct internal reforming of the biogas fuel via dry reforming. For this purpose, a long-term test was conducted to find out the SOFC's stability by supplying rich-quality biogas while the cell was maintained at 800°C. Total power remained stable over a period of 525 hours, clearly demonstrating the stable performance of the advanced SOFC technology.

The total power output from a stack containing multiple number of cells was extrapolated based on the power output measured from a single cell. However, typical stack construction will usually result in ~10% lower power due to the losses associated with series connections between the SOFCs in addition to thermal

and flow gradient throughout the volume of the stack. Figure 4 shows this projected power output along with the expected power after losses. The red line represents the projected power output from the stack as a function of temperature after extrapolating from a single cell measurement. The expected power output after losses is shown as a green line in the same plot. Based on these observations, it is possible to achieve 400+W at temperatures above 700°C and at a power density of >500 mW/cm² while supplied with biogas fuel at different compositions.

Conclusions and Future Directions

A new SOFC fabrication route was successfully implemented. This process offers numerous benefits over conventional methods: cost-effective; automated; light-weight fuel cells; and high energy efficiency.

- SOFCs with high volumetric (3.4 kW/liter), gravimetric (2.56 kW/kg) and specific power densities (0.63 W/cm²) were fabricated and tested on hydrogen and biogas.
- SOFCs demonstrated up to 50% and 40% electrical efficiencies on hydrogen and biogas, respectively.
- Different biogas compositions were evaluated on the multi-layer SOFC via internal reforming at temperatures of 700-800°C.
- SOFCs demonstrated good resistance to thermal shock, thermal cycling and showed stable performance for >500 hours of continuous operation on biogas.

The major focus for the remainder of the project will involve design, construction and evaluation of a 400 W stack on both hydrogen and biogas. All of the reporting obligations, most notably the final report, will be fulfilled.

FY 2009 Publications/Presentations

1. P.K. Cheekatamarla and C.M. Finnerty, “Biogas Fueled Solid Oxide Fuel Cell Stack” presented at the 2009 DOE Hydrogen Program Annual Merit Review and Peer Evaluation Meeting, VA, May 22, 2009. Presentation: fc_49.

V.I.10 Development of kW Scale Coal-Based Solid Oxide Fuel Cell Technology*

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Contract Number: DE-FC36-08GO0881114

Project Start Date: 06/01/2008
Project End Date: 05/31/2012

*Congressionally directed project

will develop a technological basis for the scale up of power generation capability of a kW SOFC to megawatt scale. A current density of 100 mA/cm² at 0.4 V was the initial target for demonstration of a carbon-based SOFC.

Accomplishments

Year 2009 was focused on the following milestones:

- The activity of Ni-anode for electrochemical oxidation of solid carbon was investigated at 850°C. CO was the major product of this reaction. Cu and Ce oxide will be added to the Ni-anode to increase the selectivity of CO₂ to more than 80% in the products of carbon electrochemical oxidation reaction.
- 500 h of stable operation of Ni-anode, LSM (lanthanum strontium manganese) cathode and a low-cost interconnect was achieved for H₂ fuel. Durability test for low ash carbon fuel will be conducted.
- Power density of 0.18 W/cm² at 0.4 V was achieved at 850°C for low ash carbon fuel. A further improvement of the power density for carbon-based fuel will be the focus.
- Fabrication equipment for developing large-scale fuel cell components has been purchased and tested. Fabrication variables such as slip quality and heating cycles will be evaluated
- Fabrication of coal injection and fly ash removal system has been initiated.

Introduction

The direct use of coal in the SOFC to generate electricity is an innovative concept for electric power generation. The coal-based fuel cell could offer significant advantages: (i) minimization of NO_x emission due to its operating temperature range of 700 – 1,000°C, (ii) high overall efficiency because of the direct conversion of coal to CO₂, (iii) the production of a nearly pure CO₂ exhaust stream for the direct CO₂ sequestration, and (iv) low investment and maintenance cost due to simplicity of the process. This technology also promises to provide low cost electricity by expanding utilization of U.S. coal supplies and relieving our dependence on foreign oil.

A small-scale coal fuel cell system including coal injection and fly ash removal parts will be fabricated. The main objectives of this project are (i) improvement of anode catalyst structure and the interface between

Objectives

Develop a kilowatt scale coal-based solid oxide fuel cell (SOFC) technology. The outcome of this research and development effort will form the technological basis for developing a megawatt scale coal-based SOFC technology. Objectives for 2009 included the following:

- Evaluate the anode and cathode catalyst activity and a low-cost interconnect durability.
- Investigate the factors governing the anode catalyst activity for the electrochemical oxidation of coal.
- Refine the coal injection and fly ash removal systems.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Multi-Year Research, Development and Demonstration Plan:

- (A) Durability
- (B) Cost
- (C) Performance
- (E) System Thermal Management

Technical Targets

This project is directed at the development of a kilowatt scale coal-based SOFC technology. This project

electrodes and electrolyte, (ii) developing and refining the coal-based fuel cell fabrication techniques, and (iii) fabrication and testing of a small-scale coal fuel cell system. Successful development of this novel coal fuel cell technology will significantly enhance energy security of the U.S. and bridge the gap between a fossil fuel-based economy and the future hydrogen-based economy.

Approach

Anode supported fuel cells were fabricated by tape casting procedure and tested in a steel reactor with a gas inlet port, a coke feeding mechanism, and a gas exhaust outlet port connected to the mass spectrometer and an off-stream gas chromatograph injection port. Prior to testing of the fuel cell, current collection components were attached to the cathode and Ag paste was coated along the perimeter of the anode to enhance the contact between anode and steel reactor. The performance of the fuel cell is determined by introducing the fuel (H_2 , coke and coal) and monitoring the current produced at a certain load applied to the fuel cell. A voltage-current polarization plot is also recorded under these conditions for comparison purposes.

Low cost reactors, interconnects, and current collectors based on alloy were tested for durability, stability, and efforts were focused on exploring the processes with high-volume manufacturability for producing fuel cells. A variety of tests were performed to optimize the fuel cell fabrication process, and an optimized process is currently practiced at our fuel cell manufacturing facility. X-ray fluorescence, scanning electron microscopy and energy dispersive X-ray spectroscopy techniques are used to characterize the fuel cell for analyzing the microstructure, before and after the fuel cell testing and monitoring the reproducibility of the fuel cells fabricated in-house. Low- and high-ash content coal and coke were tested for the voltage-current performance and energy conversion efficiency for carbon-based fuel was also calculated. Once sufficient understanding was gained for the (i) reaction mechanism of electrochemical oxidation of carbon-based fuel on the anode, (ii) anode microstructure in terms of porosity, tortuosity and stability, (iii) fuel cell fabrication procedure, (iv) interconnect durability and stability and (v) coal feeding, efforts were expanded to the development of new anode catalysts, fuel cell fabrication methods, and current collection assemblies for kW stack fabrication.

Results

In the past year, the main focus remained on finding a low-cost interconnect material, enhancing the power density of the fuel cell for H_2 and carbon-based fuel, determining the energy conversion efficiency and enhancing the long term stability of the fuel cell performance.

Figure 1 shows the impedance and voltage-current performance plots of a low-cost interconnect at 800°C over a 500 h period during stability testing for H_2 fuel. An ohmic resistance of $3.8\ \Omega\text{cm}^2$, polarization resistance of $7\ \Omega\text{cm}^2$ and power density of $0.11\ \text{W}/\text{cm}^2$ were recorded initially. The power density of the cell increased to $0.22\ \text{W}/\text{cm}^2$ after 122 h due to a complete reduction of NiO to Ni under H_2 , further confirmed by decrease in the ohmic and polarization resistance to $1.1\ \Omega\text{cm}^2$ and $1.5\ \Omega\text{cm}^2$, respectively at 240 h. The current density continued to decrease after 122 h to 410 h and became constant at $0.17\ \text{W}/\text{cm}^2$ till 509 h. No decrease in the ohmic resistance was observed on the impedance plot after 240 h indicating a stable performance of the low-cost interconnect material. The

FIGURE 1. Impedance and voltage-current polarization plots for the stability testing of a low-cost interconnect at 800°C under H_2 fuel.

polarization resistance increased after 240 h showing microstructure of the anode became less porous and resulted in a concentration polarization which led to decrease in the maximum power density. A decrease in porosity could occur from sintering of the anode after long-term exposure at 800°C and led to decrease in the power density till 410 h.

Figure 2 shows the voltage-current polarization plots of (a) He(50 cc/min)/low ash carbon fuel and He/H₂(80/80 cc/min)/low ash carbon fuel at 800, 825 and 850°C. A power density of 0.05 W/cm² was produced at 800°C for low ash carbon fuel which increased to 0.18 W/cm² at 850°C and did not improve after further heating to 860°C. This result shows that a high activation energy pathway exists for the electrochemical

FIGURE 2. Voltage-current polarization plots of (a) He(50 cc/min)/low ash carbon fuel and (b) He/H₂(80/80 cc/min)/low ash carbon fuel at 800, 825 and 850 and 860°C over Ni/yttria-stabilized zirconia anode.

oxidation of carbon at the Ni-anode at 800°C which was lowered at 850°C. Addition of a catalyst is necessary for enhancing the electrochemical oxidation of carbon at 800°C producing power comparable to 850°C. The power produced by low ash carbon has surpassed our 2009 goal of producing 64 mW/cm² at 0.4 V. The power produced by low ash carbon mixed with H₂ was significantly higher than low ash carbon which did not improve significantly on increasing the temperature from 800 to 850°C. This result suggests that H₂ is easier to be electrochemically oxidized than carbon at the anode, and reaches a performance level limited by the microstructure of the anode. Low ash carbon seems to be a promising fuel for SOFC technology.

Figure 3 presents the mass spectrometry profiles at the exhaust of the reactor and current produced at 0.56 V during electrochemical oxidation of Ohio #5 coke at 800°C. The information presented in Figure 2 was used to calculate the energy efficiency, as it is described in the following section. The thermodynamic efficiency ξ_T was obtained by relating w_e , the electrical work performed by the fuel cell, and the enthalpy change of the oxidation reaction ΔH . The electrical work w_e was calculated based on the current produced by the cell at the operating voltage resulting in 102.8 J. The enthalpy change of reaction ΔH was estimated considering the amount of CO₂ produced based on the gas chromatograph results, and the coke lower heating value resulting in 204.2 J. The thermodynamic efficiency ξ_T was calculated as:

$$\xi_T = \frac{102.8 \text{ J}}{204.2 \text{ J}} = 50.3\%$$

A similar energy conversion efficiency was calculated for the low ash carbon which resulted in 58.6% on the lower heating value basis of coke.

Conclusions and Future Directions

- Stable performance for 500 h of a low-cost interconnect has been demonstrated with H₂ fuel and air.
- Maximum power density of 0.18 W/cm² achieved at 850°C for low ash carbon.
- Thermodynamic efficiency of more than 50% has been demonstrated for a carbon-based SOFC at 800°C.

The proposed future research would be focused in the following directions:

- Identification of the catalyst composition for a long-term electrochemical oxidation of solid carbon fuels at 800°C.

FIGURE 3. Mass spectrometer profile and current produced vs time plot for Ohio #5 coke SOFC at 800°C.

- Further investigation of low-cost interconnects materials which cost 50% less than the present available interconnects.
- Completion of design of the fuel cell stack and testing of a small-scale (1-10 kW) coal fuel cell system.
- Fulfill reporting obligations and preparing manuscripts for publications and conference presentations.

FY 2009 Publications/Presentations

1. 2009 DOE Hydrogen Program Review – Washington, D.C. – May, 2009.

Patents Issued

1. “Catalyst Compositions for Use in Fuel Cells,” U.S. Patent Application, filed by the University of Akron on Sept.13, 2006.

V.I.11 Extended Durability Testing of an External Fuel Processor for SOFC*

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Contract Number: DE-FG36-08GO88113

Project Start Date: January 9, 2009

Project End Date: October 31, 2010

*Congressionally directed project

Objectives

The main goal of this project is to perform extended durability testing of the External Fuel Processor for the Rolls-Royce Fuel Cell Systems (RRFCS) 1-MWe solid oxide fuel cell (SOFC) power plant concept. The specific objectives are to:

- Conduct long-term tests in relevant environment of the External Fuel Processor.
- Determine long-term performance of critical components including catalysts, sorbents, heat exchangers, control valves.
- Evaluate the impact of ambient temperatures (hot and cold environments) on performance and component reliability.
- Determine system response and performance of process controls for transient operation.
- Identify any failure mechanisms.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells Section of the Hydrogen, Fuel Cells and Infrastructure Technologies (HFCIT) Program Multi-Year Research, Development and Demonstration (RD&D) Plan:

- (A) Durability
- (C) Performance

(G) Start-up and Shut-down Time and Energy/Transient Operation

These barriers will be addressed as they relate to the External Fuel Processor subsystem in the RRFCS 1-MWe SOFC power plant concept. The External Fuel Processor subsystem uses pipeline natural gas and air to generate all gas streams required by the fuel cell power plant for start-up, shut-down, low-load and normal operation. Thus it eliminates the need for on-site bottled gases.

Technical Targets

This project addresses Milestone 59 in the Fuel Cells section of the HFCIT Multi-Year RD&D Plan. Milestone 59 is to “evaluate fuel processing subsystem performance for distributed generation against system targets for 2011.” These targets will be addressed as they relate to durability, performance (gas quality - sulphur in product stream), and transient response.

Characteristic	Units	2005 Status	DOE 2011 Targets	RRFCS 2011 Targets
Cold start-up time to rated power @ -20°C ambient	minutes	<90	<30	<30 from standby
Transient response time (for 10% to 90% power)	minutes	<5	1	1
Durability	hours	20,000	40,000	8,000
Survivability (min and max ambient temperature)	°C °C	-25 +40	-35 +40	-35 ^a +40 ^a
Sulfur content in product stream	ppbv (dry)	<10	<4	<80 ppb

^a as limited by ambient conditions

Approach

The approach for this project focuses on using full-scale components from the External Fuel Processor. It includes the following:

Conduct demonstration tests in relevant environments for:

- Synthesis-gas subsystem for multiple startups and 1,200 hours of operation in a heated indoor test enclosure.

- Start-gas subsystem for multiple startups and 200 hours of steady-state operation in an outdoor test facility (hot and cold environments).
- Desulfurizer subsystem for 8,000 hours in an outdoor test facility (hot and cold environments).

Perform post-test inspections on:

- Subsystem components (catalysts, sorbents, piping, reactors, insulation, valves, heaters, heat exchangers, N₂-membrane, etc.).
- Deposits, signs of wear, damage, corrosion, erosion, and any failed components. Perform functional checks where possible.

Accomplishments

The project was initiated in January 2009. By the end of the second quarter of 2009 the following tasks were completed:

- Draft Hydrogen Safety Plan issued for comments.
- Completed mechanical installation of synthesis-gas subsystem in test enclosure.
- Confirmed operation of enclosure safety system.
- Electrical wiring for control system completed.
- Control software written and debugged.
- Specifications for outdoor test facility issued.

Future Directions

2009

- Complete synthesis-gas subsystem durability test (Fiscal Year 2009 Q3).
- Complete post-test inspections (FY 2009 Q4).
- Complete installation and commissioning of start-gas and desulfurizer subsystems (FY 2009 Q3).
- Being durability testing of start-gas and desulfurizer subsystems (FY 2009 Q4).

2010

- Complete durability testing of start-gas and desulfurizer subsystems (FY 2010 Q3).
- Complete inspections of start-gas and desulfurizer subsystems (FY 2010 Q4).
- Issue final report for project (FY 2010 Q4).

FY 2009 Publications/Presentations

1. Presentation at 2009 Hydrogen Program Annual Merit Review Meeting, M. Perna.
2. Presentation at 2009 Project Kickoff Meeting, M. Perna.

V.J.1 Diesel-Fueled SOFC System for Class 7/Class 8 On-Highway Truck Auxiliary Power

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Contract Number: DE-FC36-04GO14318

Subcontractor:
Protonex, LLC, Broomfield, CO

Project Start Date: September 1, 2004
Project End Date: December 31, 2009

Objectives

Design, develop, and demonstrate a practically sized, diesel-fueled solid oxide fuel cell (SOFC) auxiliary power unit (APU) configured to provide electrical power for sleeper cab auxiliary loads of on-highway trucks to meet the requirements for cost, size, weight, fuel efficiency, and operation on diesel fuel.

- Develop ultra-low sulfur diesel (ULSD) fuel processor.
- Develop fuel cell that operates on ULSD catalytic partial oxidation (CPOX) reformat.
- Design, build and test APU under real-world conditions.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

(A) Durability

(B) Cost

(C) Performance

Technical Targets

This project is to develop APU systems for heavy truck applications to reduce idling of the main engine. Analysis and design(s) of fuel cell APU systems will lead to the build and test of an APU demonstration unit. The projected characteristics of the proposed system differ from the DOE solicitation targets. The planned CPG-Protonex LLC products (2006 and 2010), and market expectations were derived from our belief that the primary obstacle for market entry is economics – a combination of installed cost and operating efficiencies that demonstrate a payback in the 18-24 month time frame. Secondary factors are service interval, noise and vibration, weight, and size. In order to get “on the truck” we believe the APU needs to be in the range of 8 cubic feet (225 L), weigh less than 400 lbs (180 kg), and provide a base load of about 2,500 W to service heating and air conditioning loads. Smaller size and lighter weight, while desirable, are not supported by higher price potential, nor do they justify incremental development cost or capital investment. However, under this solicitation, we believe we can leverage our Solid State Energy Conversion Alliance SOFC development work to produce a diesel-fueled SOFC APU that will meet or exceed the performance required to be commercially successful in this market. The following lists the current DOE 2010 auxiliary power units and truck refrigeration unit targets and the actual 2006 proposal targets in ()s:

Cost:	\$400/kWe	(\$1,500/kW)
Specific power:	100 W/kg	(17 W/kg)
Power density:	100 W/L	(8 W/L)
Efficiency @ rated power:	35% LHV	(25% LHV)
Cycle capability:	150 cycles	(10 cycles)
Durability:	20,000 hours	(1,500 hours)
Start-up time:	15-30 min	(60 min)

(LHV – lower heating value)

Accomplishments

- Fabricated complete modules and operated these modules on both hydrogen/nitrogen mixtures and on reformed liquid fuels.
- Thermally self-sustaining operation of complete modules was demonstrated.

- Completed the design and analysis of the power unit enclosure and complete balance of plant (BOP).
- Tested an inexpensive waste heat recovery exchanger that provides very high effectiveness at all operating conditions ($\geq 95\%$) and very low pressure drop (< 2 " water on gas side) under all operating conditions.
- Designed and programmed a custom 6-layer printed circuit board (PCB) for interfacing and control of SOFC stacks and BOP components.
- Demonstrated the complete power electronics, inverter/battery charger/direct current (DC) boost system with a fuel cell power source simulator.
- Vibration tested a complete fuel cell module at 0.5 g over a frequency range of 5 Hz to 200 Hz in three directions.

Introduction

With the onset of anti-idling legislation and the rising cost of fuel one potential early adopter for SOFC fuel cell technology is the on-highway truck APU application. First, an SOFC APU could provide the same electrical source as a conventional internal combustion engine-based APU. Second, it has the potential to improve exhaust emissions, fuel efficiency, reduced transmitted noise and vibration, and heating for both cabin and engine.

This project is directed at designing, building and demonstrating a ULSD-fueled SOFC APU installed in an on-highway truck to supply alternating current (AC) power for cabin loads, engine heating, and battery charging during rest periods.

Approach

The plan to complete the objectives of the project include identifying the overall truck system performance, power electronics, heating, battery, fuel cell system, and fuel cell hot zone requirements. Voice of Customer surveys will be used to identify and quantify the overall truck system requirements. This will flow down into detailed specifications for each sub-system/component. These specifications will be utilized to develop an overall system design that will detail the performance requirements for all sub-systems.

The APU design uses a novel dry CPOX reformer that requires no water. The APU is a modular design, based on four ~600 W (gross) modules, yielding ~2 kW net DC power. The scale up of fuel cell modules to 600 W and the development of the diesel CPOX reformer will be accomplished by modifications to a current 250 W product. Cummins Power Generation is responsible

for project management, system design, packaging, all cold BOP equipment including air and fuel supply and metering, vibration isolation, power electronics and controls. Protonex is building the hot modules, including stacks, reformers, heat exchangers, tail-gas combustors and insulation packages.

Results

In 2009, we fabricated complete modules and operated these modules on both hydrogen/nitrogen mixtures and on reformed liquid fuels. In addition to tests of full-scale stacks and modules, we also tested sub-scale modules and fuel processor components.

Each module in the APU is a complete, independent hot zone containing a tightly-integrated stack, fuel processor, recuperative heat exchanger and tail-gas combustor inside an insulation package. The stacks use 66 tubes, each 10x135 mm. Typical performance of a module on a 50% H_2/N_2 mixture is shown in Figure 1. Figure 2 shows a photograph of one of the modules. The first modules were delivered to Cummins Power Generation in the third quarter of Fiscal Year 2009.

The system uses a novel dry CPOX reformer capable of efficiently processing ULSD. During this fiscal year, we demonstrated long-term operation of the reformer using both vaporizer and atomizer feed systems. Stable operation of the CPOX for more than 500 hours between maintenance was demonstrated, with no carbon deposition on the CPOX with oxygen-to-carbon (O/C) ratios as low as 1.1. We observed carbon deposition in downstream stack and hot zone components for O/C ratios below 1.2; an O/C ratio of 1.3 was chosen for system operation. At this O/C ratio, we have been able to demonstrate more than 500 hours of stable continuous operation of reformers and subscale stacks.

FIGURE 1. Stack Load Curve on H_2/N_2 Mixture

FIGURE 2. Photograph of Module

Thermally self-sustaining operation of complete modules was demonstrated this fiscal year. Target operating temperatures can be achieved at less than 45% of target fuel flows, corresponding to a “hot idle” condition; we do not anticipate difficulties in achieving target temperatures at full power and fuel flow rates.

In FY 2009, we began testing sub-scale stacks on liquid fuels to determine the proper setpoints for the fuel processor and cathode air flow to enable reliable start-up and shut-down of stacks on liquid fuels. These tests included operation on both ULSD and low-sulfur kerosene fuels. Each thermal cycle was between 180°C and 720°C with heating and cooling times of approximately 40 minutes each. The power was very stable over these cycles, with less than 1% power loss over 10 thermal cycles. This is excellent thermal cycling performance, particularly given these relatively rapid heating and cooling rates. Although these tests were conducted with a sub-scale stack, they used a full-scale fuel reformer, so they provide a complete test of the fuel processor and a high-fidelity simulation of the conditions inside a full-scale module.

Also in FY 2009, Protonex continued work on atomizers for feeding fuel to the modules. Two fuel feed technologies are being developed in this project: fuel vaporization and fuel atomization. Fuel vaporization is currently more mature and has been selected for the initial demonstrations on this project, but atomization has the potential for longer maintenance intervals. During FY 2009, we demonstrated atomizers capable of achieving very small droplet sizes with low feed pressures. Low feed pressures are required to minimize the pumping power required to feed the fuel and air to the CPOX reactor. Compared to state-of-the-art

nozzles, this atomizer achieves small droplets at less than one-fifth the pressure drop. Low feed pressure is critical to minimizing the parasitic power draw of the fuel feed system; at a design pressure of 12 kPa, this atomizer would consume only 5% of the stack gross power while producing droplets with a Sauter mean diameter ($D[3,2]$) of $\sim 24 \mu\text{m}$. The current atomizer design operates well over a limited range of fuel and air flows. In the remainder of the project we plan to implement design changes that will extend the operating range to include startup and shutdown conditions.

Cummins Power Generation completed the BOP air delivery system fabrication for the four fuel cell module. The system includes one cathode air blower, one CPOX air boost blower, four cathode flow control valves, four anode control valves, and eight air mass flow sensors. The system achieved the required flow rate, flow adjust response time, and flow measuring resolution. A 3-dimensional printer was incorporated and significantly accelerated the air manifold and flow control valve fabrication and allows Cummins Power Generation to use low cost automotive components in the fuel cell development application.

A custom designed 6-layer PCB for interfacing and control of SOFC stacks and BOP components was completed. A Freescale microcontroller was selected as the computing core of each control board. SOFC specific software was written for execution on these microcontrollers which implemented the required operating steps outlined by Protonex.

Cummins Power Generation revised the power electronics topology after further investigation determined that the DC-DC boost was not necessary. The revised topology has the SOFC stack directly inverted to AC using a modified, Cummins Power Generation commercially produced, hybrid DC/AC/inverter/battery charger. In addition to an overall simpler topology, system efficiency has been improved 3-4% by removing the losses caused by the earlier DC-DC boost.

The sheet metal housing consists of an inner (Figure 3) and outer frame with vibration isolators in between the two frames. The inner frame has two compartments (or sides) – the hot side (or module side) which consists of the fuel cell modules and waste heat exchangers and the cold side (or BOP side) which consist of blowers and pumps (for air and fuel handling respectively) and control boards.

Stress analysis was conducted in ANSYS® using Cummins internal standard. A load of 5 g was applied in the longitudinal, transverse and vertical directions of the APU frame (longitudinal being parallel to the truck rail). The stress plots were studied and the sheet metal frame was reinforced as appropriate. In order to have high structural rigidity to weight ratio, square tubes ($\frac{3}{4}'' \times \frac{3}{4}''$) were used as structural members. The stresses in the

FIGURE 3. Fuel Cell – Inner Frame

longitudinal direction were found to be the most critical. In order to have sufficient room for the inner frame to sway inside the APU box (especially at low frequencies) a swaying clearance calculation was performed. Military standard 810 was used as a reference. The maximum accelerations and displacements at the extreme points of the frame at all operating frequencies were determined and appropriate vibration isolation mounts were selected.

Identified and tested a group of inexpensive waste heat recovery exchanger designs that provide the required cab heating with an effectiveness of $\geq 95\%$ and pressure drop of $< 2''$ water over the required range of operating conditions. Tests were conducted on the heat exchangers by simulating the fuel cell exhaust using an in-house designed and fabricated natural gas

burner. The simulated exhaust gas flow was adjusted to nominal operating conditions of the fuel cell and the temperature of the stream was 600°C which is typically the temperature reached by SOFC exhaust at the exit of the module. From a previous study it is known that the cab requires about 5 kW of heat during a peak winter event. The heat exchanger is capable of transferring the required amount of heat at a very high effectiveness at all flow conditions.

A 66-cell stack was tested at room temperature as a preliminary test to capture the module's vibration behavior. The tests were performed in the 5~200 Hz frequency range in three directions with vibration level of 0.5 g. Test results showed the fuel cell stack module had fairly symmetric vibration behavior about its vertical axis. With the current mounting design the module demonstrated a resonant peak at frequency about 75 Hz.

Conclusions and Future Directions

- This year we have fabricated complete modules and operated them on both hydrogen and reformed liquid fuels.
- We have demonstrated the viability of a dry CPOX approach at the stack and module level.

Future work

- Build and test full-scale bundles and complete 4-module sets for testing.
- Extend atomizer operating range to include start-up and shut-down conditions.
- Complete conceptual design of higher-power (~ 1 kWe) module.
- Complete SOFC APU unit fabrication and demonstration.

V.J.2 Solid Oxide Fuel Cell Development for Auxiliary Power in Heavy Duty Vehicle Applications

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Contract Number: DE-FC36-04GO14319

Subcontractors:

- Electricore, Inc., Valencia, CA
- Volvo Trucks North America (VTNA), Greensboro, NC
- PACCAR, Inc., Mt. Vernon, WA

Project Start Date: September 1, 2004

Project End Date: April 30, 2010

Multi-Year Research, Development and Demonstration (RD&D) Plan:

- (A) Durability
- (B) Cost
- (C) Performance
- (G) Start-up and Shut-down Time and Energy/Transient Operation

Technical Targets

This project is directed at the development and demonstration of a SOFC APU for heavy truck (Class 8) applications to reduce idling of the main engine. If successful, the project will address the following DOE technical targets as outlined in the HFCIT Multi-Year RD&D Plan:

TABLE 1. Auxiliary Power Units (3-5 kW rated, 5-10 kW peak)

Characteristic	Units	2010/2015 Targets ¹	Delphi 2009 SOFC APU Status ²
Specific Power	W/kg	100/100	15
Power Density	W/L	100/100	12
Efficiency @ Rated Power ^a	%LHV	35/40	35
Cost ^b	\$/kW	400/400	665
Cycle Capability (from cold-start) Over Operating Lifetime	number of cycles	150/250	125
Durability	hours	20,000/35,000	4,660
Start-Up Time	min	15-30/15-30	120

^a Electrical efficiency only – does not include any efficiency aspects of the heating or cooling likely being provided.

^b Cost based on high-volume manufacturing quantities (100,000 units per year).

¹ From Table 3.4.8 (page 3.4-19) of the DOE Hydrogen, Fuel Cells & Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan.

² Based on reported data to DOE Solid State Energy Conversion Alliance Phase I deliverables for a natural gas-based SOFC system.

LHV – lower heating value

Objectives

To demonstrate a solid oxide fuel cell (SOFC) auxiliary power unit (APU) capable of operating on low sulfur diesel fuel, in a laboratory environment, for the commercial trucking industry.

- Design and develop a SOFC APU that will increase fuel and overall system efficiency of Class 8 long-haul trucks.
- System and subsystem shock and vibration limits will be studied and recommendations made in the final report, which will address methods of isolation of the APU system to these parameters.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells – Portable Power/APUs/ Off-Road Applications section of the Hydrogen, Fuel Cells and Infrastructure Technologies (HFCIT) Program

Accomplishments

- Completed the design and layout of the enhanced superior performing DPS3000D Diesel SOFC APU to include: next generation stack design with an increased active area, enhanced thermal energy management controls, endothermic reformer integration, multi-function heat exchanger, integrated reformate desulfurizer, fully integrated

turnkey system, simplified integrated component manifold, and serviceability enhancements.

- Successful fuel reformer development of a recycle-based endothermic diesel reformer.
- Enhanced geometry packaging and modified the APU profile for mounting on heavy-duty truck chassis.
- Completed development of the DPS3000D test chassis, with integration of endothermic reformer and gaseous desulfurizer, and testing using 2007 specification diesel fuel.
- Modified natural gas platform to operate on diesel fuel for the truck demo chassis test.
- Completed a 15-hour continuous test and demonstration of a diesel-fueled SOFC APU mounted on a Class 8 Peterbuilt Model 386 truck.
- Completed development and initial testing of the development and test stands for the DPS3000D.
- Successfully performed accelerated vibration and durability testing of stack equal to 100,000 vehicle miles.
- Initiated full-scale modeling and fabrication of the APU components and hardware.
- Completed an accelerated truck load testing in the test chamber for the new process blower.

Introduction

Delphi Automotive Systems, LLC (Delphi) has teamed with heavy-duty truck original equipment manufacturers (OEMs) PACCAR Incorporated (PACCAR), and Volvo Trucks North America (VTNA) to define system level requirements and develop a SOFC-based APU. The Delphi team has enlisted Electricore, Inc. to serve as administrative manager for the project.

The project defines system level requirements, and subsequently designs and implements an optimized system architecture using an SOFC APU to demonstrate and validate that the APU will meet system level goals. The primary focus is on APUs in the range of 3-5 kW peak for truck idling reduction. Fuels utilized will be low-sulfur diesel fuel.

Approach

Delphi has been developing SOFC systems since 1999. After demonstrating its first generation SOFC power system in 2001, Delphi has partnered with Volvo Trucks and PACCAR Inc., to develop and demonstrate a SOFC-based APU for heavy truck applications.

Delphi utilized a staged approach to develop a modular SOFC system for low-sulfur diesel fuel and Class 8 truck applications. First, Delphi gathered APU

requirements from heavy truck manufacturers including VTNA and PACCAR to develop specific technical goals for the APU. Following this, Delphi continued the development and testing of major subsystems and individual components as building blocks for the APU. The major subsystems and individual components were then integrated into a “close-coupled” architecture for integrated bench testing. Delphi took additional steps to refine the overall APU and each of its components. Specialized test stands were designed and developed to test the APU enhancements and system functionality.

Results

In the past year Delphi has focused on refining and enhancing the overall APU system design and performing detailed system and subsystem testing. Specifically, work has focused on the SOFC APU hardware design and build, subsystem test fixture hardware build, and subsystem testing and development iterations. Highlights include:

- Design and development of the next generation enhanced DPS3000D APU.
- Full-scale component modeling and build.
- Next generation stack design and development.
- Completion of specialized test stands for testing the DPS 3000D.
- Initial testing of the APU system and subsystems in accordance with test plan.
- Initial vibration and durability testing.
- 15-hour continuous test and demonstration of a diesel-fueled SOFC APU mounted on a Class 8 Peterbuilt Model 386 truck.

SOFC APU Hardware Design and Build

Delphi has made significant progress in 2009 on the hardware enhancements for the next generation diesel SOFC APU, the DPS3000D (see Figure 1). These enhancements have focused on increasing the power level to 3.0 kW net with improved cooling environment around the stacks, reducing the pressure drop of components to minimize parasitic loads, improving efficiency by using an “endothermic” reformer and high recycle flow, and increasing insulation thickness and thermal component compartmentalization to reduce heat loss. Full-scale modeling and fabrication of subsystem components has also progressed in 2009. Figure 2 shows the full-scale modeling and components that have been built.

Power Electronics and System Controls

Development continued on the power electronics tray for integration on the DPS3000D. The power electronics were validated by testing conducted by

FIGURE 1. Diesel SOFC APU Conceptual Design

FIGURE 2. Full-Scale Modeling and Manufactured Components

Virginia Tech. Significant progress on the system controls, including a beta version of an optimized control code. The software was deployed on a natural gas SOFC system for initial testing.

Vehicle Interface and Diagnostics Vehicle Interface Hardware

Delphi obtained mounting information from multiple heavy-duty commercial truck OEMs in order to analyze how the APU will mount to the truck chassis.

It was necessary to consider a variety of different truck faring designs and styles to insure that operation on the trucks is possible. Effort was made on geometry packaging and modifying the APU profile in order to clear the fairings

Subsystem Test Fixture Hardware Build

Delphi has completed building multiple test fixtures to be able to conduct component and subsystem level testing. These test fixtures simulate other subsystems,

FIGURE 3. Rapid Thermal Cycle Test Stand

system inputs (i.e. diesel from the truck fuel tanks), and the environment (i.e. system heat). Figure 3 shows the rapid thermal cycle test stand.

Subsystem Testing and Development Iterations

Testing of the DPS3000D subsystems has progressed through 2009. Highlights include initial testing of the hot zone build module and initial testing of the new process air blower and recycle pump manufactured by R&D Dynamics to Delphi specifications utilizing state-of-the-art air bearing technology.

Conclusions and Future Directions

Delphi's SOFC development is recognized as being among the best performing, compact, cost-effective and durable SOFC system and stacks available today. In the 2008/2009 calendar year, Delphi has done the following:

- Achieved a major breakthrough in durability by demonstrating accelerated vibration and durability testing of SOFC stack equivalent to 100,000 vehicle miles.
- Developed and demonstrated system and subsystem testing utilizing custom design and built specialized test stands.
- Completed full-scale modeling and build of subsystems.

For the remainder of project, Delphi will complete the development, build and testing of the DPS3000D SOFC Diesel APU system and subsystems. The future direction is to continue developing the next generation SOFC system for commercial volume production introduction.

FY 2009 Publications/Presentations

1. April 2009: DoE Critical Milestone #3 Review; Rochester, NY.; Presentation: "Solid Oxide Fuel Cell Development for Auxiliary Power in Heavy Duty Vehicle Applications, Milestone Update"; Presented by: Gary Blake, Delphi Corporation.
2. May 2009: DOE Hydrogen Program Peer Review; Arlington (Crystal City), VA.; Presentation: "Solid Oxide Fuel Cell Development for Auxiliary Power in Heavy Duty Vehicle Applications"; Presented by: Steven Shaffer, Delphi Corporation.

V.J.3 Solid Acid Fuel Cell Stack for APU Applications*

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Contract Number: DE-FG36-08GO88099

Subcontractors:

- California Institute of Technology, Pasadena, CA
- Richard Mistler, Inc., Yardley, PA

Project Start Date: July 15, 2008

Project End Date: July 15, 2010

*Congressionally directed project

Objectives

The primary objective of this project is to demonstrate the feasibility of solid acid fuel cells (SAFCs) for auxiliary power units (APUs), capable of operating on low-sulfur diesel fuel and other equivalent reformat.

- Demonstrate the functionality of SAFCs on a variety of reformat including methanol, commercial liquid propane gas, and commercial ultra-low sulfur diesel fuel.
- Scale up and demonstrate the functionality of a 125 cm² SAFC membrane electrode assemblies as the platform for a 300 W SAFC stack.
- Design and model the necessary stack components including bipolar plates, seals, end plates, and hardware.
- Build and characterize the performance of a SAFC stack scalable up to 300 W.
- Generate a conceptual design for a 3 kW diesel SAFC power plant.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program (HFCITP) Multi-Year Research, Development and Demonstration (RD&D) Plan:

- (A) Durability
- (B) Cost
- (C) Performance

Technical Targets

This project is directed at the development and demonstration of a SAFC stack as an APU sub-component for heavy truck usage to reduce idling of the main combustion engine. If successful, the project will address the following DOE technical targets as outlined in the HFCITP Multi-Year RD&D Plan:

TABLE 1. Progress towards Meeting Technical Targets for APU and Truck Refrigeration Units

Characteristic	Units	2010/2015 System Targets ^a	2009 SAFC Stack Status (20 cm ² cells)
Specific Power	W/kg	100/100	36
Power Density	W/L	100/100	86
Efficiency @ Rated Power ^b	%LHV	35/40	55
Cost ^c	\$/kW	400/400	TBD
Cycle Capability over Operating Lifetime	number of cycles	150/250	20
Durability	hours	20,000/35,000	1,000
Start-up Time	minutes	15-30/15-30	45-60 ^d

^a From Table 3.4.8 (page 3.4-19) of the DOE HFCITP Multi-Year RD&D Plan.

^b Electrical efficiency only – does not include an efficiency aspects of the heating and cooling likely being provided.

^c Cost based on high-volume manufacturing quantities (100,000 units per year).

^d Start-up time based on system modeling and conceptual design.

LHV - lower heating value

TBD - to be determined

In this project we are conducting fundamental studies of SAFC tolerances to impurities found in fuel processors used to generate hydrogen-containing fuel gases. Information from these studies can be applied toward the design of stationary and portable fuel processors that meet or exceed the DOE 2011 technical targets found in Table 3.4.6 (page 3.4-18) of the DOE HFCITP Multi-Year RD&D Plan shown in Table 2.

TABLE 2. Progress towards Meeting Technical Targets For Tolerances To Impurities Found In Fuel Processors

Characteristic	Units	2005/2011 Targets	Superprotonic 2009 SAFC tolerances to impurities found in fuel
CO content in product stream ^a			
Steady-state	ppm	10/1	>200,000 ^b
Transient	ppm	100/25	>200,000
H ₂ S content in product stream	ppbv (dry)	<10/<4	>50,000,000 ^c
NH ₃ content in product stream	ppm	<1/<0.1	>100

^a Dependent on stack development (CO tolerance) progress.^b Superprotonic's SAFC stack is stable running on fuel with >20% CO.^c Superprotonic's SAFC stack is stable running on fuel with >100 ppmv H₂S.

Accomplishments

- Demonstrated the functionality and stability of the SAFC stack running on synthetic reformat with 10% CO and 100 ppm H₂S.
- Demonstrated the functionality and stability of the SAFC stack running on methanol reformat with 6.8% CO and 10.2% CO₂.
- Demonstrated the functionality and stability of the SAFC stack running on commercial liquid propane gas (LPG) reformat with 10.6% CO, 9.84% CO₂, 0.24% CH₄, 0.005% C₃H₈, and 0.5 ppm H₂S.
- Successfully demonstrated the functionality and stability of the SAFC stack running on diesel reformat with 14% CO, 10% CO₂, 0.3% CH₄ and 1 ppm H₂S.
- Fabricated higher surface area membrane electrode assembly (MEA) and tested several 125 cm² SAFC units to establish a platform for a 300-3,000 W stack.
- Designed and modeled a 300 W SAFC stack based on the 125 cm² MEA platform.

Introduction

SAFCs operate at an intermediate temperature range (230-280°C) and thus offer an attractive compromise between the advantages and disadvantages of low and high temperature fuel cells. Perhaps the most significant advantages of operating a fuel cell at these intermediate temperatures is the effective utilization of a multitude of reformed fuels, including alcohols such as methanol and butanol, and fossil fuels like natural gas

and diesel without the complexity of high temperature operation. SAFCs do require humidification but only in the gaseous phase which allow for a simpler water management system. To date, we have demonstrated SAFCs operating on hydrogen/oxygen with peak power densities of over 640 mW/cm² at an operating voltage of 0.6 V and lifetimes greater than 1,000 hours at the cell level. At the stack level, we have operated the SAFC stack on a wide range of reformat including methanol, LPG, diesel, and kerosene.

The project aims to demonstrate the commercial viability of SAFC technology and addresses many of the key DOE technical barriers and targets for enabling fuel cells as an attractive power source. The primary focus is on APU applications in the range of 300-3,000 W peak for truck idling reduction. The fuel of interest is diesel with low sulfur content.

Approach

To achieve the project objective of developing a SAFC stack capable of running on diesel reformat with the necessary performance, stability, and durability as set by the DOE for APU applications, we need to thoroughly evaluate the SAFC using air as the oxidant and a variety of reformates as the fuel. This includes synthetic reformat as well as reformed commercial fuels with high level of impurities, such as CO, CO₂, and H₂S, typically found in fuel processors used to generate hydrogen-containing fuel gases. Accordingly, initial efforts were focused on extensive physicochemical characterization of the SAFC stack on air along with synthetic, methanol, LPG, and low sulfur diesel reformates.

Once sufficient understanding was gained from the characterization, the effort was expanded to scaling up the MEA fabrication to higher surface areas for commercial applications. Two parallel approaches are being used for the scale-up: 1) electrolyte densification via cold-pressing techniques based on a modified version of the current method and 2) a completely new MEA fabrication process with densification of the electrolyte based on roller compaction techniques. Design and modeling of a 300 W stack will also take place along with the MEA scale-up activities. In addition, a conceptual design for a 3 kW SAFC power plant will be generated based on information learned from the MEA scale-up and 300 W stack design.

Results

In the past year Superprotonic has focused on characterization of SAFC stack performance on synthetic reformat and reformed fuels such as methanol, LPG, and diesel. These evaluations are very important for addressing the durability barriers and technical targets for tolerances to impurities found in

fuel processors. The tests were performed using 20 cm² MEAs in 10-cell and 20-cell stack configurations.

For the first evaluation, we used a synthetic reformat with 50% H₂, 40% N₂, 10% CO, and 100 part-per-million H₂S. The fuel and oxidant gas humidity was set at about 0.3 bar water vapor pressure using two separate PermaPure™ humidifiers. We ran the stack for approximately 16 hours to test its stability under exposure to carbon monoxide and hydrogen sulfide. At the beginning of the evaluation, we obtained polarization curves with pure hydrogen as well as the synthetic reformat for comparative purposes. At the end of the 16-hour experiment, we repeated the polarization curve sequence to evaluate the stack performance after exposure to CO and H₂S. As shown in Figure 1, there is an approximately 17% drop in the fuel cell stack performance when we switched from pure hydrogen to synthetic reformat. This drop may be the result of dilution and/or slight differences in the hydrogen content of the synthetic reformat. In other words, the equivalent amount of hydrogen in the synthetic reformat may be lower than the pure hydrogen. However, more importantly, there is essentially no difference in fuel cell stack performance before and after exposure to CO and H₂S, based on the polarization curves and power density data. Results for the reformed methanol fuel evaluation are shown in Figure 2. The reformat flow rate was 2.8 standard liter per minute (SLPM) to provide an equivalent flow rate of 1.0 SLPM hydrogen. The composition of the methanol reformat was 74.2% H₂, 6.8% CO, and 18.2% CO₂. Owing to the higher hydrogen content, the effect of hydrogen dilution is not as strong as the case with the synthetic reformat.

FIGURE 1. Polarization curves for pure hydrogen fuel (pink square) and synthetic reformat fuel (blue cross) before and after 16 hours of exposure to CO and H₂S (hydrogen - navy blue dash, reformat – brown circle). The power density data also suggest there is no adverse effect due to CO and H₂S.

For the reformed propane fuel evaluation, we also used a 20-cell stack made up of 20 cm² SAFCs. The fuel and oxidant gas humidity was set at about 0.3 bar water vapor pressure using two separate PermaPure™ humidifiers. The reformed fuel was obtained with a propane steam reformer running at approximately 650°C. The reformat fuel flow rate was 5.8 SLPM to best approximate an equivalent flow of 1.0 SLPM H₂. We evaluated both “pure” LPG as well as commercial LPG available at vendors such as The Home Depot. The composition of the pure propane reformat was 40.4% H₂, 34.4% N₂, 10.8% CO, 9.5% CO₂, and <1% of other byproducts such as CH₄ and C₃H₈. The composition of the commercial propane reformat was 41.1% H₂, 34.6% N₂, 10.6% CO, 9.84% CO₂, <1% of other byproducts such as CH₄ and C₃H₈, and 0.5 ppm H₂S. There are four time points of interest in the experiment. At time points 1, 2, 3, and 4 we ran the SAFC stack on 1.0 SLPM H₂, 5.8 SLPM pure LPG reformat, 1.0 SLPM H₂, and 5.8 SLPM commercial LPG reformat, respectively. At all time points, we obtained polarization curves after switching the fuel at the anode. After the fourth polarization scan, we ran the stack steady-state on a 1 ampere direct current load for approximately 4 hours. After the steady-state run, we acquired another polarization scan for comparative purpose. Figure 3 summarizes all polarization scans from the propane reformat evaluation. The purpose of the polarization scans at time points 1 and 3 on pure hydrogen is to establish baselines for evaluating the SAFC stack performance on the two LPG reformates. The results from the evaluation suggest a very slight drop in performance when we switched from pure hydrogen to reformed LPG fuels. Based on the composition of the reformat, we believe most of the reduction in power density and stack voltage is the result of hydrogen dilution. These results suggest that the SAFC possesses

FIGURE 2. Polarization curve from a 20-cell SAFC stack running with pure humidified hydrogen (blue data) and reformed methanol fuel (red data). There is a slight reduction in performance possibly due to dilution.

FIGURE 3. Polarization curves from the evaluation of SAFC stack on liquid propane gas reformat. The solid data points are power densities and the unfilled data points are electric potentials.

excellent fuel compatibility with commercial liquid propane gas reformates.

The fuel of choice for APUs in the trucking industry is low-sulfur diesel. Accordingly, for the final portion of the flex-fuel evaluation, we ran a SAFC stack on hydrogen fuel processed from a bench-top diesel auto-thermal reformer. The exit of the reformer was connected to the inlet manifold of the stack anode with a tubular, air cooled heat exchanger in between. The stack anode inlet manifold allowed the operation of the stack on either a H_2 gas or the reformat gas stream. Diesel fuel was purchased from a local gas station with a total sulfur content of 400 ppm by weight. The tests were conducted first by using pure H_2 as the fuel for the stack to obtain stack baseline polarization (IV) curves. We then switched to the reformat at flow rates approximately equivalent to the corresponding pure H_2 flows. The reformat composition was analyzed using a gas chromatograph (GC) to confirm its product distribution. Based on the GC measurement, the diesel reformat contained 41% N_2 , 35% H_2 , 14% CO , 10% CO_2 , 0.3% CH_4 , and 1 ppm H_2S by volume. The oxygen-to-carbon ($O_2:C$) and water-to-carbon ($H_2O:C$) ratios were 1:2 and 2:1, respectively. After running the stack on diesel reformat for a few minutes for stability purpose, we collected the stack IV curves to compare with the data to the pure H_2 runs. Figure 4 illustrates a polarization curve comparison between hydrogen and low-sulfur reformat. It is important to note that the hydrogen content for the diesel reformat was only 35% and the pure hydrogen fuel used for comparison purpose in Figure 4 was not diluted down to these percentages. In addition, the CO and CO_2 contents at 14% and 10%, respectively, for the diesel reformat were higher than expected.

FIGURE 4. Polarization curves for a SAFC stack running on diesel fuel reformat (pink lines) compared to pure hydrogen (blue lines).

Overall, our evaluation of the SAFC stack on reformed fuels yielded positive results. These results suggest that byproducts, such as CO , CO_2 , CH_4 , and H_2S , from reformed fuels such as methanol, LPG, and diesel had minimal adverse effect on the SAFC stack performance with hydrogen dilution being the dominant mechanism for reduction in power output.

In order to demonstrate the commercial viability of the SAFC, we also need to increase the MEA surface area to a size that will allow us to achieve the targeted specific power and power density shown in Table 1. For this project, this equates to fabricating an MEA with surface area greater than 100 cm^2 to establish a platform for the 300 W stack. In the past year, we demonstrated the ability to fabricate a functional 125 cm^2 SAFC MEA using existing equipments. However, at approximately 47 mW/cm^2 , the power density of these MEAs is not as high as the 20 cm^2 MEA version but we expect to be able to markedly improve the performance with better equipment and optimized electrolyte.

Complementary to the 125 cm^2 MEA fabrication, we also designed and modeled the 300 W stack. Using a conservative value of 120 mW/cm^2 for the cell power density, we expect to operate 20 125 cm^2 cells at a cell operating voltage of 0.7 V. The stack weight and volume are 10 kg and 2.8 liter, respectively. The exaggerated weight of the stack is due to the fact that we used machined stack components. We expect the stack weight will reduce greatly as we transfer to high-volume manufacturing processes.

In terms of modeling, we simulated the gas flow and pressure distribution for the individual bipolar plate flow field and a simplified model of a 20-cell 300 W SAFC stack. For the bipolar plate, we used FloWorks, finite element analysis plug-in module for Solidworks. In a fuel cell stack, the bipolar plate functions as the support

for the MEA, fuel and oxidant supplier, and conductivity medium. The modeled 7075 aluminum bipolar plate, with a thickness of 0.125 inch (0.3 cm), consisted of fuel cell flow field, heat exchange flow field, and manifold. The flow field diameter is 5 inches (12.7 cm) with an area of 19.625 in² (126.6 cm²). The flow pattern of the bipolar plate would affect the flow distribution and fuel mass transport; thus, a good flow field design should have uniform flow distribution at high velocity with low pressure drop. The boundary condition for the bipolar plate simulation is as follows:

- Temperature of humidified air: 20°C was used to study bipolar plate flow field.
- Inlet volume flow: 100 sccm per minute.
- Outlet static pressure: 101,325 Pascal.

Our computational modeling results of the fuel flow field gas flow and pressure distribution suggest that our bipolar plate design should allow for good uniformity of gas flow at high flow velocity throughout the MEA. The pressure drop from the inlet to the outlet is relatively small (<0.2%).

We also modeled the gas flow velocity and pressure distribution in a stack configuration using a commercially available computational fluid dynamics software package called *CFdesign*. The purpose of this simulation was to determine cell-to-cell gas flow uniformity. In our model, the SAFC stack consists of the gas manifolds, two end plates and twenty 125 cm² bipolar plates. The primary function of the manifold is to supply gas for flow field of each fuel cell, which in a stack, plays a very important role in controlling gas flow uniformity. Factors such as area, shape and length of manifold would affect the pressure drop and cell-to-cell flow distribution. Generally, the smaller pressure drop in manifold and bigger pressure drop in flow field would provide a more uniform flow distribution of cell-to-cell. Non-uniform cell-to-cell flow distribution may lead to fuel starvation which would affect stack performance and durability. In the stack model, the flow field consists of four channels, each with a channel depth of 0.035 inch and a width of 0.0425 inch. Owing to computation limits, we had to simplify the flow field and replaced the serpentine channels with shorter straight channels with the same cross section. The channel length varies between 5.5 to 6 inches. The inlet flow to each cell was set at 200 SCCM.

From the stack simulation, we can conclude that the pressure drop is greatest in the gas tube leading into the manifold. Within the manifold, the pressure profile is relatively flat for both the inlet and outlet manifold. Since the pressure profile is flat both at the inlet and outlet manifold, we can also conclude that the pressure drop between inlet and outlet is the same for all cells. This behavior should lead to good uniformity of gas distribution throughout the stack. It is important to

note that we expect, in an actual stack with longer flow field channels, the bigger pressure drop due to the longer channel would lead to more uniform flow distribution. In other words, the flow distribution should be better in an actual stack than that of our model. For comparison, we simulated a case with a much higher flow rate at 10 liters per minute. The higher flow rate provide a larger pressure drop from the inlet to the outlet manifold across the flow field channels. As predicted, the cell-to-cell velocity distribution is more uniform with high flow rate as compared to low flow rate.

Conclusions and Future Directions

Superprotonic's SAFCs constitute a transformative technology for cost-effective mass adoption of the fuel cell. SAFC MEAs, with a solid-state proton conducting electrolyte layer, operate at an intermediate temperature of approximately 250°C, and are impermeable to gases. These electro-physical properties afford SAFCs a clear advantage over existing fuel cell technologies in term of cost, durability, fuel flexibility, thermal cycling, and simplified system design. In the past year, Superprotonic has completed the following:

- Demonstrated stable stack operation on synthetic reformat with >10% CO, 100 ppm H₂S, and 100 ppm NH₃.
- Demonstrated stable stack operation on methanol and LPG using a steam reformer.
- Demonstrated stable SAFC stack operation on diesel using an auto-thermal reformer.
- Scaled-up the MEA surface area from 20 cm² to 125 cm².
- Completed the design and modeling of a 300 W SAFC stack.

For the remainder of the project, Superprotonic will continue to optimize the MEA performance to levels of commercial viability, demonstrate the functionality of a SAFC stack at in the 300 W range, and complete a conceptual design of a 3 kW SAFC power plant running on diesel fuel.

FY 2009 Publications/Presentations

1. 2009 DOE Hydrogen Program and Vehicle Technologies Program Annual Merit Review and Peer Evaluation Meeting – Washington, DC – May 2009; Presentation FC_45: "Solid Acid Fuel Cell Stack for APU Applications", Presented by Hau H. Duong, Superprotonic, Inc.

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V.J.4 Research & Development for Off-Road Fuel Cell Applications

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Contract Number: DE-FC36-04G014303

Subcontractors:

- The Toro Company, Bloomington, MN
- University of California (UC Davis), Davis, CA

Project Start Date: August 9, 2007

Project End Date: June 9, 2010

Technical Targets

Conduct field trials at River's Edge Golf Course and The High Desert Museum (HDM) Wildlife and Living History.

Accomplishments

- Measured the shock, and vibration spectrum for golf course maintenance vehicles.
- Gathered information on the air contaminants that may have an effect on fuel cell operation and developed an air filter for fuel cell systems.
- Developed the Workman[®] e2065 lawn tractor equipped to operate on direct current (DC) voltages, and had accelerometers installed and evaluated shock and vibration.
- Measured the power load profiles on two golf courses.
- Designed and installed an IdaTech liquid-fueled fuel cell system in a Toro Workman[®] e2065 light-duty maintenance truck.
- Re-designed and installed an IdaTech liquid-fueled fuel cell system in a Toro Workman[®] MDE light-duty maintenance truck.
- Continue field trials with two vehicles.

Objectives

- Develop system to allow proton exchange membrane (PEM) fuel cells to operate in off-road applications.
- Evaluate air-filtration technologies for off-road applications.
- Conduct a program of study, evaluation and laboratory testing needed to establish a comprehensive set of PEM fuel cell system requirements for turf and grounds maintenance vehicles.
- Fully integrate prototype PEM fuel cell system in a Toro Workman[®] e2065 – series utility vehicle for field trials.
- Conduct field trials utilizing two vehicles.
- Demonstrate vehicle at various venues.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

(A) Durability

Introduction

Nearly no practical work has been performed by the fuel cell industry, and its suppliers and trade associations on the subject of off-road fuel cell operation. The environments encountered in off-road applications could adversely affect fuel cell performance and life, requiring re-designing for the harsher environment.

One of the recognized challenges in fuel cell systems air purification is in providing a highly efficient particulate and chemical filter with minimal pressure drop. PEM integrators do not want additional parasitic loads added to the system as compensation for a highly efficient yet highly restrictive filter. Additionally, there is challenge in integrating multiple functions into a single air intake module tasked with efficiently and effectively filtering high dust loads, diesel soot, pesticides, ammonias, high frequency noise, and other anticipated off-road contaminants.

It is one key project objective to develop a strategy, and through it a solution, for achieving clean cathode inlet air. Other off-road concerns are related to fuel cell power requirements and the effect of shock and vibration.

Approach

- Measure the air quality for off-road application and develop an air filter.
- Measure the shock and vibration spectrum for off-road vehicles, and then subject an IdaTech fuel cell system to the spectrum.
- Design, assemble, and test a Toro Workman® e2065 light-duty maintenance truck with an IdaTech liquid-fueled (methanol/water) fuel cell system incorporating the developed air filter.

Results

An IdaTech liquid-fueled fuel cell system was assembled, tested at IdaTech, delivered to UC Davis and demonstrated at UC Davis. Shake and vibration testing has begun at UC Davis and six of eight tasks completed.

Toro has determined the fuel cell systems specification for the Workman® e2065 and IdaTech's FCS 3000 system meets the specifications and incorporates the developed air filter. A Toro Workman® e2065 light-duty maintenance truck was received, and designated test vehicle (TV)-1.

Three fuel cell systems were assembled and all three passed operational testing. One unit while sitting next to the vehicle was used to charge the battery configuration. The unit was reconfigured and installed into the vehicle. The vehicle has accumulated 63.5 hours of off-road operation at the River's Edge Golf Course. A photo of TV-1 on the golf course is shown in Figure 1. During the summer of 2008, TV-1 accumulated 62 hours of maintenance duties. During the winter an upgrade was performed on the fuel cell system. Wiring connections were reduced, a smaller lighter DC to DC converter on a studier sheet metal support and onboard data acquisition were incorporated. Every ten seconds data is stored on a replaceable memory card. The installed upgraded fuel cell system is shown in Figure 2. TV-1 has accumulated the following statistics:

Fuel Cell Run Time = 171 hours
 Total Fuel Feed = 465 liters
 Total Energy = 353 kW/hr
 Total Thermal Cycles = 165

A second vehicle, designated TV-2, was procured from Toro which Toro has designated as an MDE model (mid-duty electric). The new vehicle design incorporates front wheel shocks and an accessible area under the front hood. An upgraded fuel cell system was installed in the vehicle. The batteries were placed two in front and two in the rear compartment. This eliminated the "saddle bag" batteries external to the rear compartment in the first vehicle. The vehicle rear compartment was modified to provide ease of removal of the whole

FIGURE 1. TV-1 on Golf Course

FIGURE 2. Upgraded IdaTech Liquid-Fueled Fuel Cell System Installed in TV-1

system for maintenance. Onboard data acquisition was added. Every ten seconds data is stored on a replaceable memory card. The fuel cell system installed in TV-2 is shown in Figure 3. The second vehicle was deployed at HDM south of Bend, Oregon. This field trial differs in that the terrain is flatter, the operators more educated and the vehicle will accumulate more operating hours. The vehicle in front of the HDM is shown in Figure 4. TV-2 has accumulated the following statistics:

Fuel Cell Run Time = 315 hours
 Total Fuel Feed = 77 liters
 Total Energy = 42 kW/hr
 Total Thermal Cycles = 51

The present systems have four generic printed circuit boards installed. Many of the functions on the boards are not used with the present system. Many wires could be eliminated by consolidating the four boards onto one board. We have contracted with Etrix Group Inc. a local electronic design company, to consolidate the needed functions onto one board.

FIGURE 3. IdaTech Liquid Fueled Fuel Cell System Installed in TV-2

FIGURE 4. TV-2 at the High Desert Museum

Conclusions and Future Directions

The work conducted so far shows that an IdaTech liquid-fueled fuel cell system can be integrated into an off-road vehicle. Operation on a real golf course atmosphere was successful; however, improved reliability is required. Some example of faults and corrections:

- System over-heated on very hot day – added cooling fan.
- Thermocouple shorted – added restraint.
- Wires fell off coolant switch – restrained wires.
- Fuel pump slowed down, dirt was cause – sealed pump gearbox opening.
- Fuel line dry – removed tank dip tube and place exit at tank bottom.
- Inverter not ramping up – installed improved inverter and improved firm ware.
- Troubleshooting faults takes too much time – added onboard data acquisition.
- Multiple printed circuit boards with unused capability and extra connectors increase wiring breakage – consolidation of board recommended.

Field trials will continue for both vehicles. Demonstrations of the vehicles will be scheduled for the rest of the project.

FY 2009 Publications/Presentations

1. Annual Merit Review: fcp_03_lawrance

V.J.5 Direct Methanol Fuel Cell Prototype Demonstration for Consumer Electronics Applications

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Contract Number: DE-FC36-04GO14301

Subcontractor:
Methanol Foundation, Arlington, VA

Start Date: August 1, 2004
End Date: March 2009

Multi-Year Research, Development and Demonstration Plan:

- (A) Durability
- (B) Cost
- (C) Performance

Technical Targets

Target metrics for the sub-Watt to 50 W fuel cell system category are shown in Table 1. Some of the targets are not applicable to the sub-Watt systems. These systems will not have the power and energy density or cost of a larger system in this category. The metrics defining a market introduction point for sub-Watt systems can be obtained from analysis of the power source currently used for the targeted application. Commercially available rechargeable Li-Ion battery-based power packs are used to charge handheld electronic devices on the road. The emergence of these products signals a market need and an entry point for handheld fuel cells. These power packs have an energy density of about 100–150 Wh/liter with a fully charged battery. This energy is even lower if one takes into consideration the volume of the wall charger. Fuel cell products under development for this market need only to be significantly better than these battery-based chargers to be successful. This project and subsequent product programs are on track to achieve all the metrics needed to make a direct methanol fuel cell (DMFC) for handheld electronics a commercial success, helping to clear the path for similar hydrogen fuel cell-powered device introduction.

TABLE 1. Progress toward Meeting Technical Targets for sub-Watt to 50 Watt Category

Characteristic	Units	DOE 2006/2010 Targets	2008 MTI Status
Specific Power	W/kg	100	NA
Power Density	W/L	100	NA
Energy Density	Wh/L	1,000	600*
Cost	\$/W	3	NA
Lifetime	Hours	5,000	>1,000**

*Projection based on using a large cartridge/tank with average performance from 18 DOE systems tested in Q4 2009

**Testing completed on P2 prototypes in 2007/2008

NA - not available

Objectives

- Develop an early pathway for the large-scale public introduction to fuel cell benefits.
- Demonstrate 1,000 hours of continual operation at a system level.
- Demonstrate overall energy density equal to or better than 600 Wh/L.
- Accelerate codes and standards activities that allow shipping and use of methanol and their cartridges in airline passenger cabins.
- Develop straight-forward refueling with 100% methanol, possible while source is on.
- Prepare three successive generations of benchmark prototypes (P1, P2, P3) to evaluate system integration issues and validate performance and life.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells, and Infrastructure Technologies Program

Approach

- Develop system designs that reduce complexity, size, and number of components.
- Use 100% methanol fuel (undiluted) to maximize energy density.
- Passively manage water to optimize power, efficiency, and size.
- Work with original equipment manufacturers to develop product introduction strategy, getting them familiar with fuel cell characteristics and advantages.
- Accelerate codes, standards, and regulations to allow shipping and airline passenger cabin usage.
- Develop supply chain, teaching fuel cell technology to suppliers as appropriate.

Accomplishments

- Achieved 1,000-hour target of system operation on multiple units completing this key project objective.
- Built and tested 18 P3 integrated prototypes demonstrating performance, life, orientation independence, and 0-40 degrees Celsius temperature latitude.
- Membrane electrode assembly (MEA) power and life achieving product requirements. Achieved over 6,000 hours of operation with less than 30% degradation.

Introduction

DMFC technology and MTI's passive Mobion[®] implementation is well-suited for handheld portable power applications in consumer electronics such as cell phones, cameras, smart phones, personal digital assistants, and game systems. It uses a liquid methanol fuel directly, instead of hydrogen, so that issues associated with converting the liquid fuel to hydrogen and then managing the hydrogen gas are avoided. This, along with the lower costs associated with the smaller platform, allows the DMFC technology to proceed at a faster development pace than the related hydrogen fuel cell technology. An early introduction of fuel cells into the consumer environment will assist the development of the necessary manufacturing base for all fuel cell technologies to follow and will gain a broader public understanding of the fuel cell merits.

Approach

The overall technical approach MTI has used from the beginning of this project has been to reduce the number of components needed in a typical DMFC system. MTI focused on reducing the complexity of the anode loop and water recovery from the cathode stream. These two systems are interrelated because of water management. MTI's fuel cell is designed in such a way that there is a net water transport from cathode to anode through the membrane. This is a passive process that requires no energy. This results in a simplified DMFC system as shown in Figure 1.

FIGURE 1. MTI Simplified DMFC System

FIGURE 2. P3 DMFC Prototype System with Removable Methanol Cartridge

Results

The work completed under this project has significantly increased the understanding of how DMFCs can be deployed successfully to power consumer electronic devices. The prototype testing has demonstrated the benefits a direct methanol fuel cell system has over batteries typically used for powering consumer electronic devices. The universal charger developed in-part by this project is an early pathway for the large scale public introduction to fuel cell benefits.

Three generations of prototypes have been developed and tested for performance, robustness and life. The technologies researched and utilized in the fuel cell stack and related subsystems for these prototypes are leveraged from advances in other industries such as hydrogen fueled PEM fuel cell industry. The work under this project advanced the state-of-the-art of direct methanol fuel cells. The system developed by MTI Micro Fuel Cells aided by this project differs significantly from conventional DMFC designs and offers compelling advantages in the areas of performance, life, size, and simplicity.

The project has progressed as planned resulting in the completion of the scope of work and available funding in December 2008. All 18 of the final P3 prototype (see Figure 2) builds have been tested and the results showed significant improvements over P2 prototypes in build yield, initial performance, and durability. The systems have demonstrated robust operation when tested at various orientations, temperatures, and humidity levels.

Durability testing has progressed significantly over the course of the project. MEA, engine, and system level steady-state testing has demonstrated degradation rates acceptable for initial product introduction. Over 5,000 hours of test duration have been achieved at both the MEA and breadboard system level. Figure 3 shows

FIGURE 3. MEA Life Test Demonstrating over 6,000 hours of Operation with less than 30% Decay

an MEA life test demonstrating over 6,000 hours of operation with less than 30% decay.

P3 level prototype life testing on engines showed degradation rates comparable to carefully constructed lab fixtures. This was a major improvement over the P2 and P1 engine designs, which exhibited substantial reductions in life and performance between the lab cell and the actual engine.

Over the course of the work on the P3 technology set, a platform approach was taken to the system design. By working in this direction, a number of product iterations with substantial market potential were identified. Although the main effort has been the development of a prototype charger for consumer electronic devices, multiple other product concepts were developed during the project showing the wide variety of potential applications.

Cartridge size is the major factor driving energy density of the platform. By changing the size of the fuel cartridge, the same fundamental platform design can be used with minimal changes to meet the requirements of the various markets. A small cartridge is best for the applications where the consumer carries the device on his/her body, such as an external charger for portable electronics. A large cartridge is best for applications where reducing service (fuel refills) is important. This large cartridge design is capable of long run applications, like unattended ground sensors which are currently powered by lead acid batteries. These two applications bound the extremes of the cartridge size with many other applications falling in between these bounds. Based on the 18 DOE unit's average baseline performance the energy density is projected to exceed 600 Wh/L when using the large cartridge capable of 2,000 hours of run time. The same platform equipped with a single small cartridge, can easily fit in your pocket, which makes it easy to carry, but also results in lower energy density.

There is a substantial body of regulations that govern the use and transport of hazardous materials. This project has concentrated on the international

FIGURE 4. Codes and Standards Activities and Timeline

regulations for fuel transport and fuel cell use in airline passenger cabins. Teams from MTI and the Methanol Foundation have been deeply involved in wide ranging tasks with multiple international bodies, as shown in Figure 4, driving the standards forward. Many milestones have been achieved toward acceptance of fuel cells in airline passenger cabins. In the process, a number of white papers and presentations have been prepared for U.S. Department of Transportation and Federal Aviation Administration to allow them to become familiar with the fuels and fuel cell technologies and to address their safety concerns.

Removable cartridges containing 100% methanol have been produced and have demonstrated hot swap capability on the P3 system prototype. MTI/Methanol Foundation team led efforts on life-cycle issues for methanol fuel cartridges. Meetings were held with officials from the New York State Department of Environmental Conservation in 2007 and again in late 2008 to demonstrate actual working prototypes and discuss proper “end of life” options for fuel cell cartridges and fuel cell systems.

Conclusions and Future Directions

- Achieved over 1,000 hours of runtime on multiple prototype systems and demonstrated over 5,000 hours on a P3 breadboard system.
- Tested 18 fully integrated P3 prototypes demonstrating performance, life, orientation independence, and temperature latitude.
- Removable cartridges containing 100% methanol have been tested with the P3 prototype and have demonstrated the capability of refueling while the power source remains on.
- Achieved over 6,000 hours of MEA operation with less than 30% degradation.
- No future work under this project. The project’s scope-of-work and available funding was completed in December 2008.

FY 2009 Publications/Presentations

1. Prueitt, J., Qi, Z., Lu, G., Liu, W., and Carlstrom, C., 2009, “Performance and Durability of Direct Oxidation Fuel Cells Fed with Neat Methanol,” Small Fuel Cells Conference, May 7–8, Orlando, FL.
2. Minas, C., 2008, “Structural and Thermal Design Challenges of Portable Microfuel Cell Systems,” IMEC2008-69270, ASME Congress, Nov 2–6, Boston, MA.
3. Qi, Z., Prueitt, J., Lu, G., and Carlstrom, C., 2008, “Fuel Cell Battery Hybrid Systems,” Lithium Battery & Fuel Cell Hybrid Systems Conference, December 10, Las Vegas, NV.

V.J.6 Silicon-Based Solid Oxide Fuel Cell for Portable Consumer Electronics*

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Contract Number: DE-FG36-08GO88102

Project Start Date: August 1, 2008
Project End Date: March 31, 2009

*Congressionally directed project

Technical Targets

This project is directed at the development of improved micro-SOFC chips and high-volume compatible manufacturing processes. The power, lifetime, and manufacturability improvements will be applied toward portable fuel cell systems that meet the following DOE 2010 consumer electronics targets:

- Energy density: 1,000 Wh/L
- Lifetime: 5,000 h

Accomplishments

- Established a scalable, automated fuel cell electrode dispense platform with a 10X improvement in repeatability.
- Improvements in stack array electrode adhesion increased SOFC energy density by 85%.
- Modification of the thin film stack on the silicon support structures provided an increase in operating temperature from 700°C to 750°C, resulting in a 30% power improvement.
- Incorporation of these improvements into a full SOFC chip assembly provided a 250% power improvement over the best demonstrated chip at the start of this project.

Objectives

Increase micro-electro-mechanical systems (MEMS) solid oxide fuel cell (SOFC) array power density and lifetime through process and design changes that will:

- Significantly improve the throughput and repeatability of the electrode manufacturing process.
- Improve the average power density of the SOFC array by 50%.
- Improve chip-level vacuum sealing to support operation at 800°C.
- Allow fabrication and test of SOFC devices that demonstrate realized improvements over current design.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) Durability
- (B) Cost
- (C) Performance

Introduction

Lilliputian Systems Inc. (LSI) is developing a novel miniature fuel cell for the consumer portable power market. LSI's fuel cell uses efficient SOFC technology, is manufactured using MEMS fabrication methods, and runs on high energy fuels, such as butane, hydrogen, or ethanol. The company's breakthrough Fuel Cell on a Chip™ technology enables a form-factor battery replacement for portable electronic devices that has the potential to provide an order-of-magnitude run-time improvement over current batteries.

This Department of Energy funded project focused on accelerating the commercialization and market introduction of this technology through improvements in fuel cell chip power output, lifetime, and manufacturability. To achieve these objectives, work was performed to close the gap between the higher power density demonstrated on button cell test structures and that available on stacked array die. A robust, automated electrode fabrication tool was developed to support the increased production rate required to perform array optimization. The causes of limited lifetime at elevated

temperature were investigated and improvements to the silicon die coatings were made to allow increased SOFC operating temperature. These improvements were then incorporated into a full SOFC chip assembly to benchmark the overall performance improvements realized.

Approach

Scanning electron microscopy (SEM) images of fuel cell electrode arrays indicated that significant electrode delamination was occurring on the array die. This was believed to be related to stress in the electrode introduced during the drying process. Experiments were performed investigating the effect of variations in the amount of electrode material dispensed per coat, as well as the drying and curing process profiles. In order to support increased production rate required to optimize the array electrode process, an automated electrode dispense tool was developed along with a wafer-level electrode fabrication process.

To increased chip lifetime at higher operating temperatures, glass seal improvements were necessary to reduce reactivity with the silicon support structure. Glass compositional changes, incorporation of barrier layers, and modifications to the die films were investigated.

Results

The energy density achieved on electrode test structures has historically been higher than the energy densities attained on stacked electrode arrays. The more complex physical structure of stacked arrays requires different precursor solutions and process optimization to achieve maximum power density. In order to support the large number of experiments necessary to achieve this optimization, a high-throughput manufacturing process was necessary. This new, high-throughput process also had the requirement of improving electrode consistency.

LSI had investigated commercially available deposition equipment appropriate for producing the SOFC arrays and determined that standard equipment does not have either the accuracy or repeatability necessary for fabrication of high energy density fuel cell arrays. In order to attain the necessary dispense performance, LSI has developed enhancements to equipment built and supplied by Asymtek Inc. An improved dispense volume control system was designed, built, and tested by LSI. Dispense volumetric accuracy and repeatability has been improved by greater than 20X and 10X, respectively (see Figure 1). This has resulted in improved electrode uniformity, faster processing and higher yields. Additional throughput improvement was achieved through implementation of wafer-level processing, which requires less labor than

FIGURE 1. Automated Dispense Volume Accuracy With and Without Closed-Loop Control

die-level electrode production. Experiments verifying the equivalency of the wafer-level process have been completed successfully. In addition to providing a solid foundation for the process refinements necessary to increase power density, the improved dispense equipment and wafer-level processing have established a solid platform for rapid scaling to production quantities.

SEM images of the fuel cell electrode arrays have indicated that significant electrode delamination is occurring on the fuel cell die. This is believed to be related to stress in the electrode introduced during the drying process. Experiments were performed which investigated the relationship between the amount of material dispensed per coat and the magnitude of observed delamination. Results have indicated that there is not a significant level of improvement to be gained by this approach. Experiments involving variations in drying temperature and time were performed, which resulted in observable improvements in overall electrode adhesion. Figure 2 shows an 85% increase in array power achieved through process improvements.

Increasing the fuel cell chip operating temperature improves the output power but reduces the chip lifetime. Experiments have shown that the lifetime of the current sealing glass used in the LSI fuel cell chips drops significantly between 700 and 800°C. Cross-section analysis of the glass seals by SEM and energy dispersive spectroscopy (EDS) indicates that chemical changes to the glass composition are occurring at the higher temperatures, and there is evidence that these changes are contributing to the shortened operational lifetime.

Several new glass formulations were created and analytical analyses of these glasses indicated that they crystallize more fully than current glasses, generally indicating higher reliability. Unfortunately due to delays in bringing a new high temperature furnace on-line,

FIGURE 2. Fuel Cell Array Average Power, Normalized to Average Power in July

furnace down-time due to a crucible failure, and glass incompatibility with current paste-making facilities, LSI was not able to evaluate the new glasses in complete fuel cell chip assemblies during the time frame of this project. The new glasses will be evaluated in prototype chips at a future date.

Chemical interaction between the sealing glass and the fuel cell die at elevated temperature has also been investigated through the use of SEM EDS and is a contributor to reduced seal life at higher temperatures. Several proprietary barrier layers were developed and evaluated for suitability in increasing seal lifetime at temperature (see Figure 3). Several of the tested barrier layers showed promise in reducing the reaction between the sealing glass and the silicon fuel cell die; however these materials proved difficult to integrate into the fuel cell die process flow and require substantial redesign of the MEMS chips to incorporate. The insights gained from work performed on barrier layers led to changes in the composition, stress, and thickness of the thin films originally incorporated in the fuel cell chips, and a significant improvement in seal performance was observed, as shown in Figure 4. Although the target operating temperature of 800°C was not fully attained, a significant increase from 700°C to 750°C was realized.

Fuel cell chips were fabricated with both the improved electrodes and the operating temperature enhancements. These devices were tested to benchmark performance, and these changes were shown to increase in fuel cell power by a factor of 2.5X over the maximum power demonstrated at the start of this project. These results are shown in Figure 5. This represents a major step forward in the commercialization of the LSI Micro Fuel Cell Chip technology.

FIGURE 3. Coupon Burst Strength With and Without Barrier Layer (Test pressure limit: 30 psi)

FIGURE 4. Coupon Burst Strength as a Function of Layer Thickness

Conclusions and Future Directions

The LSI MEMS-based micro-SOFC has clearly demonstrated the potential for an order-of-magnitude run-time improvement over the lithium ion batteries

FIGURE 5. Fuel Cell Chip Assembly Power, Normalized to Power in July

used in portable consumer electronics today. The progress made during this project has:

- Provided a scalable, automated fuel cell electrode dispense platform.
- Significantly improved the operating temperature and lifetime of the fuel cell chip.

- Achieved an 85% improvement in array energy density through electrode fabrication process development.
- Achieved a 30% increase in output power due to higher operating temperatures.
- Demonstrated a 2.5X increase in fuel cell chip output power.

Future work will include evaluation of the new glass compositions and revision of the MEMS design to allow incorporation of barrier layers, both to further increase operating temperature and lifetime. Fuel cell energy density will be further improved through continued refinement of the electrode fabrication process and redesign of the silicon support structure to increase fuel cell active area.

FY 2009 Publications/Presentations

1. 2009 DOE Hydrogen Program Review - Washington, D.C. - May, 2009. Presentation FC# 48.

V.J.7 Engineered Nanostructured MEA Technology for Low Temperature Fuel Cells*

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Contract Number: DE-FG36-08GO88097

Project Start Date: August 1, 2008
Project End Date: July 30, 2011

* Congressionally directed project

Project Objective

The objective of this project is to develop a novel catalyst support technology based on unique engineered nanostructures for low temperature fuel cells which:

- Achieves high catalyst activity and performance
- Improves catalyst durability over current technologies
- Reduces catalyst cost

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan (HFCIT):

- (A) Performance
- (B) Durability

Technical Targets

This project is directed at the development of durable catalysts supported by novel support that improves the catalyst utilization and hence reduce

the catalyst loading. This project will develop a solid fundamental knowledge base necessary for the synthetic effort while at the same time demonstrating the catalyst advantages in direct methanol fuel cells (DMFCs). If successful, the project will address the following DOE technical targets as outlined in the HFCIT Multi-Year Research, Development and Demonstration Plan:

This project is conducting fundamental studies of nanowire supported catalysts applied in fuel cells. Insights gained from these studies will be applied to DMFCs first to demonstrate the catalyst advantages over commercial carbon supported catalysts, prior to eventual demonstration in hydrogen fuel cells:

- $>60 \text{ mW/cm}^2$ at 40°C , ambient condition
- Demonstrate durability advantage, $<60 \mu\text{A/hr}$

Accomplishments

- Produced Si nanowire with a diameter as small as 30 nm.
- Converted Si nanowire to graphite/SiC nanowire with high surface area of $125 \text{ m}^2/\text{g}$ (Brunauer-Emmett-Teller, BET).
- Controlled Pt alloy particle size in the range of 1.5~3 nm, average 2 nm.
- Uniformly deposited Pt alloy nanoparticles on nanowire support.
- Achieved $>112 \text{ mW/cm}^2$ (2x of target) with nanowire catalysts-based membrane electrode assembly (MEA) at ambient condition and 40°C for 3M DMFCs, which is 45 mW/cm^2 better than that with a commercial catalyst.
- Achieved durability of over 1,000 hours with $9 \mu\text{V/hr}$ decay rate (equiv. 6.5x of target).

Introduction

The MEA in a fuel cell contains the catalysts critical to the process which promote the electrochemical reactions such as oxidation of hydrogen or methanol and reduction of oxygen. In today's fuel cells, the level of precious metal catalyst utilization using supported catalysts in the MEA is extremely low, around 20-30%. This low catalyst utilization represents a major barrier towards lowering the cost and improving the performance of fuel cells. Additional efficiency is lost when catalyst particles are located such that they are in poor electrolytic contact with the proton exchange

membrane or poor electrical contact with the electrode through the support matrix. Each of these elements impacts overall efficiency of the MEA and therefore the resulting fuel cell. The U.S. DOE outlined four strategies to address challenges in catalysts and support materials, which are: lower precious group metal content – improved Pt utilization and durability; Pt alloys – maintain/improve performance and reduce cost; novel support structures – non-carbon supports and alternative carbon structures; non-Pt catalysts – maintain performance and durability.

For this project, we are to develop a novel catalyst support technology based on unique engineered nanostructures for low temperature fuel cells which achieves high catalyst activity and performance, as well as improves catalyst durability over current technologies. Through precise control of the nanowire density, diameter, length, surface chemistry, catalyst deposition density and sulfonic acid group density of polymer electrolyte, we will be able to independently control and optimize each of the most important elements of the MEA, including porosity, electrical connectivity, electrolyte connectivity and catalyst accessibility. This level of control is not possible with traditional packed-bed MEAs and will allow us to fabricate MEAs in which majority of the catalyst material is accessible and active.

Approach

To achieve the objectives, novel inorganic nanowire supported catalysts are being developed by utilizing the Nanosys nanowire synthesis technology and nanoparticle synthesis technology. This includes, in particular, SiC nanowire as well as PtRu and Pt nanoparticles. This includes:

- Create nanowires using vapor-liquid-solid (VLS) synthesis method for synthesizing Si nanowires and then carburizing them to form SiC/nano-graphite core/shell nanowires;
- Create catalyst nano-particles using colloidal method;
- Integrate catalyst onto nanowire support with improved stability and activity;
- Fabricate catalyst coated membrane with nanowire supported PtRu and Pt catalysts and control the porosity of catalyst layers as well as catalyst and ionomer distribution in MEA;
- Optimize cell performance and perform durability evaluation.

Results

We have grown silicon nanowires on the surface of a substrate using a colloidal catalyst based VLS synthesis method. SiH_4 is used as the growth gas. The diameter is controlled within 30~40 nm. Then, the silicon

nanowires are directly converted at high temperature into SiC coated with nanographite shell. The nanowires have been characterized using transmission electron microscopy (TEM) and/or scanning electron microscopy. After the high temperature process the crystallinity and nanowire structure are retained. TEM studies have indicated this graphite shell is covalently bonded onto the surface of the SiC nanowires. The high crystallinity and covalent bonding between nanographite and SiC make this support much more stable than poorly crystallized carbon black. The final core-shell nanowires have diameters as small as 30 nanometers and aspect ratios of ~100:1. The rough nanographite shell makes the nanowire material have good electrical conductivity. This also results in a large surface area of ca. 125 m²/g, measured by BET.

We have prepared free-standing well-dispersed nanoparticles using a solution phase process method. By controlling the reaction temperature profile and ratio of starting reagents and conditions, the particle size, size-distribution and composition have been tuned independently. Energy dispersive X-ray analysis has confirmed the ratio of Pt and Ru is ca. 1 to 1. X-ray diffraction results indicate that the particle size of the metallic PtRu particles can be controlled from 1 to 5 nm, typically, 2 nm.

We have successfully developed a method to integrate the nanoparticle catalysts onto the nanowire supports by dispersing the nanowire support materials in ethylene glycol and then adding the nanoparticles. By inducing electrostatic attraction between the nanoparticles and the nanowires, this integration is quite strong for the relative size of the nanoparticles and nanowires. Typically 30% PtRu can be easily deposited on the nanowire support. The uniform distribution of nanoparticles on the surface of the nanowire support has been observed by TEM, as shown in Figure 1.

The activity and performance for a methanol oxidation reaction at the nanowire supported PtRu catalyst has been characterized in an electrochemical cell at 40°C. At 0.5 V, the mass current for methanol oxidation at PtRu/NW is ca. 2.5x higher than that at PtRu/C (commercial), which clearly indicates PtRu/NW advantage in activity for methanol oxidation over PtRu/C.

The stability of PtRu/NW catalyst for methanol oxidation has been measured by cycling potential between 0.05 V and 0.6 V for 3,200 cycles. The loss in mass current measured at 0.5 V (27%) is much lower than that of 69% for commercial PtRu/C catalyst under the identical condition. The losses in electrochemically active surface area are similar for both PtRu/NW and PtRu/C catalysts (~22%), which may indicate comparable defoliating and coalescing of the catalysts. We may assume the net loss in mass activity can be evaluated by the difference between the measured mass current loss and the surface area loss. Therefore, only

FIGURE 1. TEM Image for PtRu Distribution on Nanowire Support

5% loss is for PtRu/NW, which is much lower than that of 47% for the PtRu/C catalyst.

Using the nanowire catalysts, commercially available gas diffusion layers and Polyfuel hydrocarbon membranes, MEAs of 5 cm² active area are fabricated for the catalyst performance evaluation. A catalyst coated membrane method is used to fabricate MEAs. Formulation of nanowire catalyst, ionomer, and dispersion solvents have been optimized. The Nafion[®] ionomer with lower equivalent weight (EW1000) has been used for the nanowire supported catalyst.

The porosity of the nanowire supported catalyst layer is comparatively larger than that of the carbon supported catalyst layer; consequently the ionomer can be uniformly distributed in the layer with nanowire supported catalysts. In contrast, large ionomer agglomerates can be observed in the catalyst layer with carbon supported catalysts. These features result in a higher triple phase boundary (TPB) area for the nanowire supported catalysts over the carbon supported catalysts, and hence result in a higher catalyst utilization and a higher performance.

Anode polarization and fuel cell polarization performance have been evaluated. To compare and evaluate the nanowire anode catalyst, a commercial Pt/C cathode catalyst is used. The anode in an MEA made with nanowire catalyst shows that the improvement in anode polarization is ca. 47 mV at 100 mA/mg-PtRu and 71 mV at 200 mA/mg-PtRu, as shown in Figure 2. We have also achieved a maximum power density of 112 W/cm² in DMFC with nanowire anode catalyst and

FIGURE 2. Anode Polarizations for Methanol Oxidation, PtRu/NW (Nanosys) vs. PtRu/C (commercial)

FIGURE 3. Fuel Cell Polarization and Power Density (PD) Curves, PtRu/NW (Nanosys) vs. PtRu/C (commercial)

3M methanol at 40°C, which is 45 mW/cm² higher than that with commercial PtRu/C anode catalyst (68 mW/cm²), see Figure 3.

Nanowire supported catalysts have advantages over commercial carbon supported catalysts, which have high catalyst utilization (1.6x > PtRu/C), high activity (2.6x > PtRu/C), high accessibility, and high stability/durability, as shown in Table 1. These differentiate nanowire-based catalysts from carbon supported catalysts. For anode polarization, the mass current of PtRu/NW is 3.4 times

TABLE 1. Nanowire Supported Catalyst Advantages

	TPB Area (m ² /g)	Catalyst Utilization (%)	AP, I (mA/mg) @ 0.45 V, 40°C	AP, I (mA/mg) @ 0.3 V, 40°C
Nanosys PtRu/Nanowire	47	61	260	9.8
Commercial PtRu/Carbon	23	39	76	3.8

**Nanosys
Advantage**

2x

1.6x

3.4x

2.6x

AP – Anode polarization

higher than that of PtRu/C at 0.45 V, 40°C. This mass current is attributed to improvement in both activity and accessibility. In contrast, at lower potential of 0.3 V, the activity-dominant mass current for PtRu/NW is 2.6 times higher than that of PtRu/C. The difference in mass current gain between 0.45 V and 0.3 V is an indication of improvement in accessibility for PtRu/NW. In addition, we achieved durability of over 1,000 hours with 9 uV/hr decay rate, by operating the DMFC with 3M MeOH and ambient air at 40°C.

Conclusions and Future Directions

Nanosys has developed durable fuel cell catalysts, which outperform the state-of-the-art catalysts:

- The project demonstrated novel inorganic nanowire catalyst support and catalysts. This may fundamentally overcome the catalyst durability problems, in particular, carbon corrosion problem.
 - Unique features of the nanowire supported catalysts are firstly demonstrated for methanol oxidation prior to hydrogen oxidation. It turned out that PtRu/NW catalysts have higher activity, utilization and accessibility over commercial PtRu/C catalysts.
 - Nanowire supported catalysts have superior stability over carbon supported catalysts.
 - The results have been presented in 2009 Small Fuel Cells and 2009 DOE Annual Review meetings.
- For the remainder of project, we will fulfill reporting obligations, most notably the final report, and prepare manuscripts for publications. As for future directions, we will explore further applications in hydrogen fuel cells and develop more active catalysts for cathode. (This effort will continue at Nanosys after completion of the project.)

Patents Issued

1. Nanostructured Catalyst Supports, 01-007440US, filed in April of 2009, Yimin Zhu, Jay Goldman, Baixin Qian and Ionel Stefan, portions of this invention may have been made pursuant to a contract with the US DOE, Hydrogen, Fuel Cells & Infrastructure Technologies Program (# DE-FG36-08G088097).

FY 2009 Publications/Presentations

1. **DMFC Inorganic-Nano-Fiber-Based Catalyst with Superior Performance and Lifetime** *Yimin Zhu, Ionel Stefan, Baixin Qian, Jay Goldman, Jurgen Hofler and Jason Hartlove*, 11th Annual International Conference for Small Fuel Cells 2009 - May 7-8, 2009.
2. **Engineered Nanostructured MEA Technology for Low Temperature Fuel Cells** *Yimin Zhu, Ionel Stefan, Baixin Qian, Jay Goldman, Jurgen Hofler and Jason Hartlove*, 2009 DOE ANNUAL MERIT REVIEW and PEER EVALUATION MEETING, May 18, 2009; fcp_09_zhu.

V.K.1 Light-Weight, Low-Cost PEM Fuel Cell Stacks

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Project Start Date: February 28, 2007

Project End Date: August 31, 2009

Technical Targets

TABLE 1. Relevant Technical Targets for Fuel Cell Stacks and Systems Operating on Direct Hydrogen

Metric	Units	2010 target	Status*
System Specific Power	W/kg	650	1,050
Stack Efficiency at Rated Power	%	55	40
Stack Cost	\$/kW _e	25	Not Determined

*Estimated from results of single cell testing, when combined with the weight of the molded cell component.

Accomplishments

- Fuel cell results in single cell hardware, combined with the weight of the first generation of molded components are consistent with a stack power density greater than 1 kW/kg. However, adhesion and long-term stability of the printed current collector remain issues.
- We have incorporated temperature and humidity sensors within our single-cell edge collected hardware and have demonstrated that these results are in good agreement with our 2-D water transport model.

Objectives

- Demonstrate edge-collected stack design capable of >1 kW/kg (system level).
- Develop low-cost, injection molded stack components.
- Verify stack performance under adiabatic conditions.
- Develop direct humidification scheme based on printed 2-dimensional (2-D) microfluidics.
- Develop optimized printable current collectors for edge collection.
- Accelerate stack development by incorporation of multiple cell level sensors within the stack coupled with computational fluid dynamics modeling.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

(B) Cost

(C) Performance

Introduction

The benefits and limitations associated with conventional bipolar stack construction are well known. The primary benefit of bipolar construction is that it allows for low internal resistance due to the maximum conducting area between cells. It also leads to dense, highly compact stacks. However, despite considerable effort the bipolar plate still represents a daunting fabrication challenge. As a result, bipolar plates represent a sizable fraction of the weight and cost of the stack. Furthermore, they are inactive components that do not contribute directly to energy conversion. Bipolar construction has a negative impact on stack operation as well, including water management issues related to water retention in the stack (especially critical during freeze/thaw cycling), relatively high pressure drop and a large number of seals that must be maintained.

In response to these issues, a light-weight, low-cost proton exchange membrane (PEM) stack design is being developed that is responsive to DOE performance and

cost goals and that is substantially simpler in design and construction than conventional bipolar stacks. This design is based on edge collection of current and eliminates the need for bipolar plates.

Approach

The edge-collected design being pursued uses gas diffusion layers/current collectors that are fabricated by a printing process that provides intimate contact between the various components, eliminating the need for compressive forces currently used to ensure low-resistance contacts. As a result, numerous components of conventional stacks including bipolar plates, tie-rods and individual cell-level seals are eliminated, greatly reducing the parts count, weight, and assembly complexity. Low-cost, light-weight housings will be fabricated by injection molding to enclose the fuel cell components and to provide reactant manifolding. Adiabatic operation with very low pressure drop will allow for extremely low parasitic power losses due to the elimination of the compressor and substantially simpler humidification requirements. Printed microfluidic pathways (essentially 2-D wicks for introducing water directly into the stack) will be an essential element in achieving adiabatic operation. Figure 1 shows the conceptual design of a 27-cell stack (ca. 150 W), which consists of four molded plates, and three sheets of catalyst-coated membrane (CCM). The dimensions of this sub-stack are 22 cm x 15.5 cm x 1.8 cm.

Results

Our progress this year has been slowed as a result of two significant issues. The first of these is related to adhesion of the printed current collector/gas diffusion layer (GDL). Our preferred formulation for this layer, which yields our best fuel cell performance, was shown to have poor adhesion under repetitive wet/dry cycling

at 60°C. Loss of adhesion was typically observed in ≈ 30 cycles, far too few to be acceptable. As a result, a large portion of our effort has been spent on evaluating alternative formulations for this critical component, as we attempted to find an acceptable balance between adhesion, electrical conductivity and porosity. We have demonstrated a formulation (formulation 'B') with excellent conductivity and adhesion under wet/dry cycling, but with a lower than acceptable porosity. This lack of porosity is manifested in a fairly low limiting current, on the order of 200-300 mA/cm², as shown in Figure 2. Various attempts to improve the limiting current, while maintaining the required level of conductivity have not been successful.

The second major issue we have been addressing is the performance of the commercial CCM material that has been our starting point for fuel cell production. In a presentation at the FreedomCar Tech Team Review in late September 2008, we presented a number of significant issues with this material. These issues included relatively poor fuel cell performance, characterized by low open circuit potentials (ca. 0.8 V), excessive hydrogen crossover (10-20 mA/cm²), low power density, and a significant frequency of electrically shorted cells after fabrication. We have also presented results from testing in conventional fuel cell hardware, for the same CCM material, showing similar deficiencies. These results showed that to a significant extent, the poor fuel cell performance could be traced to the performance of the commercial CCM material. Since this was an unexpected result, samples of this material were sent to Los Alamos National Laboratory (Drs. R. Borup and T. Rockward) in October 2008 for evaluation at the recommendation of the Tech Team. Their preliminary results received in mid-November are in good agreement with our own. Further testing in our labs showed that the electrical shorts observed are present in the as-received CCM material, although it is

FIGURE 1. Exploded View of a 27-Cell Short Stack, Consisting of 3–9 Cell Sub-Stacks

FIGURE 2. H₂/Ar Polarization Curve For In-House Fabricated CCM with Printed Current Collector (temperature = 60°C, dry air, humidified hydrogen)

likely that our current collector fabrication exacerbated these inherent faults. As it is clear that this material will not be suitable for this project, we are currently scaling-up our in-house fabrication of the CCM. Our goal will be to produce CCM material that is more suitable for this project, which, by the nature of the edge-collected assembly used, is aimed at relatively low current density (ca. 0.4 A/cm^2) and high efficiency ($V_{\text{cell}} > 0.7 \text{ V}$) operation. The fuel cell performance shown in Figure 2 was obtained with our in-house fabricated CCM, which has an acceptable open circuit potential ($\approx 0.94 \text{ V}$), and acceptable hydrogen crossover ($\approx 1 \text{ mA/cm}^2$).

We have also continued our efforts to incorporate sensors within our edge-collected fuel cell hardware and to demonstrate that our water transport model correctly predicts local relative humidities within the cell for a variety of conditions (for example, open-circuit vs. hydrogen pump vs. fuel cell operation, and conventional reactant humidification vs. humidification via the microfluidic pathways). While these experiments are still in progress, the results to date show good agreement between the model and the laboratory results.

Conclusions and Future Directions

- **Current Collector Formulation/Fabrication:**
It is clear that we need to consider substantially different approaches to fabricating a current collector/GDL that achieves all of our targets for conductivity, porosity and adhesion simultaneously. A breakthrough in this area is necessary to achieve a viable result. Electrospraying of this layer is one such possibility.
- **Water Transport Modelling/Measurement:**
We will continue our efforts in this area in order to demonstrate the advantages that we believe will result from the edge-collected design with adiabatic operation and humidification via microfluidic pathways.

Publications/Presentations

1. A presentation was made for the FreedomCar Tech Team Review on September 24th, 2008.

V.K.2 Fuel Cell Research at the University of South Carolina*

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Contract Number: DE-FC36-06GO86041

Subcontractor:

Oak Ridge National Laboratory, Oak Ridge, TN

Project Start Date: February 1, 2007

Project End Date: October 31, 2009

*Congressionally directed project

Technical Targets

The first sub-project is developing Nb-doped TiO₂ supports for catalyst with the goal:

- Durability of electrocatalysts with cycling: 2015 target <30 mV loss after 100 h @1.2 V

The other sub-projects all relate to improving durability to achieve the durability targets of 5,000 h for transportation applications and 40,000 h for stationary applications. The second sub-project is developing an understanding of the levels of contaminants that impact automotive H₂ fuel quality. The data, models, and rate constants allow the DOE H₂ Quality team to predict performance loss mechanism and effects.

The third sub-project is providing information for the technical task associated with selecting the seal technologies in the second quarter 2011 that will allow the system to meet the durability target.

The fourth sub-project is providing information for stationary systems that allows one to assess durability at 40,000 hours and predict the time when stack power is less than 10% of the rated power.

Objectives

This project consists of four sub-projects. The primary objective of each sub-project is:

- Develop high surface-area non-carbon supported catalysts with improved corrosion resistance.
- Obtain data and rate constants for performance losses caused by fuel contaminants in support of the H₂ Quality team.
- Develop a fundamental understanding of degradation mechanisms of existing gaskets and test the performance of improved materials.
- Obtain data and develop models of polybenzimidazole (PBI)-type high temperature membranes.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) Cost
- (B) Durability
- (C) Performance

Accomplishments

- Developed a Nb-doped TiO₂ support that displays catalytic activity equivalent to Pt/C for high levels of doping.
 - The synthesized support has a mesoporous structure and a surface area of approximately 150 m² g⁻¹, which is much higher than that reported in the literature.
- Obtained anode overpotential data as required by the H₂ Quality team.
 - Data for concentrations below the fuel standard indicate 10 mV of additional polarization at 25 psig and 60°C for 0.4 mg/cm² Pt on the anode.
- Developed laboratory characterization methodologies for understanding stress relaxation, chemical stability, and leaching of contaminants for low-cost seals.
- Measured water content as a function of temperature and water partial pressure for commercial PBI membranes.

Introduction

Sub-project #1 focused on increasing the life of the electrodes in polymer electrolyte membrane (PEM) fuel cells by replacing the carbon support of the platinum catalysts with a non-corroding, inexpensive metal such as titanium oxide. This material typically has low conductivity and low surface area but if these can be overcome, it may be preferable to carbon because it does not undergo corrosion at high potentials. Sub-project #2 focused on providing data that can be used to set international specifications for hydrogen quality used by fuel cell vehicles. These specifications are important because ultra-pure H_2 will be expensive but contaminants will affect the life of the fuel cell.

The third sub-project measured the properties of low-cost seal materials to help with the selection and design of new materials. We focused on understanding the mechanisms of failure, designing accelerated measurement procedures, and quantifying the contaminants that leach from these materials and thereby decrease the life of the fuel cell. The fourth sub-project measured the properties of a high-temperature membrane that quantify its interactions with water vapor during operation of a stationary fuel cell. These properties can be used in a model to predict lifetime and failure mechanisms.

Approach

To achieve the objectives of sub-project #1, niobium-doped titania-based catalyst supports were synthesized and characterized. The characterizations included surface and spectroscopic methods, electrochemical and corrosion methods, and stability analysis and performance studies of the supports loaded with catalysts. To obtain the data for sub-project #2, we performed polarization experiments using GORE PRIMEA® Series 57 membrane electrode assemblies (MEAs) exposed to neat hydrogen and very low concentrations of CO contaminated hydrogen. Data for these commercially available electrodes complement the work of investigators at the National Renewable Energy Laboratory, Argonne National Laboratory (ANL), Savannah River National Laboratory, Los Alamos National Laboratory, and at other universities. The DOE H_2 Quality team chose CO as a “canary” indicative of the ability to clean hydrogen in pressure swing adsorption operations.

Researchers on sub-project #3 were guided by industrial members in the National Science Foundation Center for Fuel Cells [1]. In an effort to develop accelerated testing protocols, seal materials were aged at different temperatures, with and without stress and deformation, while being exposed to two different solutions. One solution simulates a beginning-of-life fuel cell environment (denoted below as a regular

solution) and the other solution contains trace chemicals that accelerate degradation and that may be present towards the end of life (denoted in the following as the accelerated testing solution). The materials were characterized for chemical stability using attenuated total reflectance Fourier transform infrared (ATR-FTIR), scanning electron microscopy, X-ray photoelectron spectroscopy, and leachant solution analysis at weekly intervals. We characterized the mechanical properties and structural integrity by measuring ductility, hardness, elastic modulus, and stress relaxation. In sub-project #4, measurement techniques were developed to rapidly measure the mass gain of PBI membranes exposed to different mixtures of water vapor and air. These techniques include in situ water balance and water accumulation experiments as well as ex situ isotherm and water accumulation experiments.

Results

In the past year for sub-project #1, the synthesis procedures (i.e., sol-gel and hydrothermal methods) have been studied in an effort to understand the interactions between the amount of dopant, the conductivity, the electrochemical surface area, and the catalytic activity. That is, as reported last year, the electrical conductivity showed a maximum for 25% Nb. Also, last year we reported that the electrochemical active surface area (ECSA) of a Pt catalyst deposited on the Nb- TiO_2 was comparable to that of Pt catalyst supported on carbon (Pt/C) and that the new supported catalyst is selective for the 4-electron reaction pathway since the maximum H_2O_2 production is 4% of the current. This year our X-ray diffraction studies indicate that the Nb acts to stabilize the anatase form of the support and that the conductivity is low for both the anatase and the rutile phases. However, these materials function well as catalysts despite the low conductivity as the weight of conductive metal (i.e., either “dopant,” coating metal, or catalyst) is increased.

This year in sub-project #2, we completed the studies of CO poisoning at concentrations that span the specification for fuel quality (i.e., 0.2 ppm). These measurements used the techniques, reported last year, appropriate to ensure steady-state reproducible data. An example of this data, reported to the H_2 Quality team, is shown in Figure 1 for the anode overpotential caused by CO contamination at 60°C at back pressures of 0/0 psig and 25/25 psig on the anode/cathode. We used the typical automotive inlet relative humidity condition of 75/25% (anode/cathode) and varied the partial pressure of CO from 10 to 0.1 ppm. This range of partial pressures is necessary to determine if the poisoning mechanism changes, to develop cell models [2], and to test models of stack recycle being developed at ANL [3-5]. We also obtained data for 80°C, which

FIGURE 1. Steady-state effects of pressure and CO concentration on the anode overpotential at 60°C for a GORE 57 Series MEA with anode/cathode (A/C) stoichiometry = 1.2/2.0 and A/C relative humidity = 75%/25%.

shows, as expected, that the polarization is less than that at 60°C.

In Figure 1 the plateaus indicative of CO oxidation appear only for concentrations of 2.5 ppm and higher. At the lower concentrations of 1 ppm, the anode overpotential may be insufficient to oxidize electrochemically the CO at cell current densities of 1.8 A/cm², indicating no electrochemical oxidation of CO and an ECSA controlled by the adsorption isotherm. Thus, any recycle loop for the fuel that results in an increase of CO to 1 ppm will result in 120 to 150 mV of polarization or voltage loss per cell at 1.8 A/cm². Figure 2 expands the scale for the 0.1-ppm data to reveal polarization of 10 mV at 25 psig and 60°C. Note the error bars of ± 5 mV for these polarizations and that we claim that these error bars are consistent with the measurement limits for data obtained from 25 cm² and 50 cm² cells.

Figure 3 shows an example of the chemical stability data obtained in sub-project #3 this year. There, the changes in the concentration of silicate are shown for the low-cost liquid silicone elastomer (DLS), the silicone copolymeric resin (DC), and the fluorosilicone rubber (DFS) for exposure in the accelerated testing solution (A-) and the regular solution (R-). The increases in the silicate leachant concentration for the A-DLS and A-DC materials correlate to the rate of change in the weight loss of these materials (not shown). ATR-FTIR analysis of the DLS material showed chemical changes in the backbone and cross-linking domains after three weeks of exposure to the accelerated testing solution and no significant changes after 15 weeks of exposure to the regular solution. Measurements of the elastic modulus for the A-DC material showed a gradual decrease over time and a significant change between 20 and after 25

FIGURE 2. Expanded view of low overpotential region of Figure 1 showing error bars and an overpotential essentially independent of current density at 0.1 ppm CO in H₂.

FIGURE 3. The change in silicate leachant concentration during 25 weeks of chemical stability testing at 80°C. The acronyms for the materials are defined in the text. A-DLS, A-DC and A-DFS correspond to samples in the accelerated testing solution and R-DLS, R-DC, and R-DFS correspond to samples exposed to the regular solution.

weeks which may correlate with the increase in silicate shown in Figure 3.

In sub-project #4 this year, we used our previously developed techniques to measure the equilibrium water content of a PBI-MEA as a function of temperature and water vapor pressure. Figure 4 shows these data and that the moles of water per mole of acid bound in the PBI structure increases sharply for temperatures of 120°C or less. This increase has implications when there are inadvertent shutdowns during operation or during laboratory testing. Heretofore, experimentalists

FIGURE 4. Effect of water vapor pressure (dimensionless by 101.3 kPa) and temperature on water content (λ = mol fraction of water/phosphoric acid) for Celtec® P Series 1000 PBI-MEAs.

were concerned about carbon corrosion of the electrode by the cathode air during shutdown or unexpected interruption of the current at high temperatures and these data indicate that low temperature excursion history also should be part of the information reported with long-term performance data for these MEAs. We also measured the rate of adsorption of water into the PBI MEA due to a step change in inlet humidity and those data show a time-constant of 500 and 2,500 seconds, respectively at 70 and 50°C. These time constants can be compared with one of less than 100 seconds for temperatures greater than 100°C. Desorption of water was slower at a given temperature.

Conclusions and Future Directions

Sub-project #1 prepared supported catalysts that have comparable activity to existing Pt/C catalysts, probably because the conductivity and the surface area was increased.

Sub-project #2 provided data not previously available and which was suitable for comparison with other MEAs over an operating range that allows parameter estimation. The data for concentrations lower than the proposed specifications allow the effect of recycle and contaminant accumulation to be assessed. We will complete this sub-project with measurements to assess the interaction of CO with NH₃ once the lower loading MEAs are provided by the H₂ Quality team.

In sub-project #3, large silicate concentrations were observed in the leachant from some low-cost seal materials with the accelerated testing solutions. ATR-FTIR successfully detected backbone and cross-linked changes prior to significant weight loss or leachant concentrations.

Sub-project #4 obtained new data characterizing the adsorption of water in a PBI membrane as a function of

temperature. These data also suggest the need to report the temperature history with durability data.

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12. J.Z. Tan; Y.J. Chao, Y. Min, C.T. Williams, and J.W. Van Zee, "Degradation Characteristics of Elastomeric Gasket Materials in a Simulated PEM Fuel Cell Environment," *J. of Materials Engineering and Performance*, **17**(6) 785-792 (2008).

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V.K.3 Center for Fundamental and Applied Research in Nanostructured and Lightweight Materials*

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Contract Number: DE-FG36-08GO88104

Subcontractor:
Clemson University, Clemson, SC

Project Start Date: July 1, 2008
Project End Date: January 31, 2010

*Congressionally directed project

- Demonstrate novel electrodynamic deposition methods (electrospinning and electrospraying) for a set of paradigm polymeric compounds in membrane form.
- Identify candidate materials for membrane synthesis using these methods.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) Durability
- (B) Cost
- (C) Performance
- (D) Water Transport within the Stack
- (E) Thermal System and Water Management

Technical Targets (Planned completion date: 1/31/2010)

- **Task 1:** Fabrication, testing, and modeling of carbon filled polypropylene composites for fuel cell bipolar plates (70% complete).
- **Task 2:** Synthesis and characterization of Pt/Ni overlayer catalysts (45% complete).
- **Task 3:** Test hybrid materials fabricated (30% complete); development of electrospraying apparatus (80% complete).
- **Task 4:** Electrospinning of hybrid electrospinning composites (40% complete).
- **Task 5:** Microscopy and spectroscopic analyses of a commercial Poco Graphite foam sample and an MTU nickel-carbon electrode (40% complete); making a graphitized carbon foam from a peroxyacetyl nitrate precursor (50% complete); active mass deposition, forming, and cycling (70% complete).
- **Task 6:** Designing a swagelok battery cell (90% complete); ethylenediamine tetraacetic acid titrations of deposited active mass (40% complete); anode preparation (50% complete).
- **Task 7:** Contact angle measurement apparatus and technique (90% complete); contact angle measurements on GDL samples (25% complete); compression fixture (95% complete); compression-force measurements on GDL samples (25% complete).

Objectives

Area 1: Heat and Water Management

- Develop and test lightweight and nanostructured materials for fuel cell bipolar plates.
- Improve gas diffusion layer (GDL) performance and durability and develop testing and characterization protocols for GDLs relative to water management.

Area 2: Development of New Electrode Materials

- Develop graphitic carbon foams that will serve as current collectors and catalytic supports.
- Develop durable carbon-supported catalysts that have reduced weight and cost compared to proton exchange membrane (PEM) anode catalysts.

Area 3: Enabling Technologies for Membrane Synthesis

- Develop hybrid polymer membrane materials which are engineered at the micro and nanoscale.

Accomplishments

Area I: Heat and Water Management

- Developed a material containing 2.5 wt% AkzoNobel KetjenblackEC-600 JD carbon black/65 wt% Asbury Carbons ThermocarbTC-300 synthetic graphite particles/6 wt% Hyperion carbon nanotubes/26.5 wt% Dow homopolymerpolypropylene H7012-35RN:
 - Electrical conductivity: obtained 91 S/cm (DOE target is 100 S/cm) via compression molding and 38 S/cm via injection molding.
 - In plane thermal conductivity: obtained 24 W/m²K (DOE target is >20 W/m²K) via compression molding and 18 W/m²K via injection molding.
 - Studied movement of water in fuel cell electrodes:
 - Environmental chamber fabricated.
 - Second level thermostat design completed and fabrication started.
 - Analysis code completed.
 - Contact angle measurement error characterized.

Area II: Development of New Electrode Materials

- Synthesized graphitic carbon foams at Clemson University.
- Studied the structure and morphology of carbon foam electrode supports.
- Performed battery tests with synthesized electrodes.
- Synthesized pseudomorphic nanoscale overlayer bimetallic catalysis as an alternative to platinum-based fuel cell anode catalyst.

Area III: Enabling Technologies for Membrane Synthesis

- Developed novel polymer electrospinning/electrospinning apparatus.
- Created three distinct variable diameter scaffolds by manipulating electrospinning parameters.
- Developed fluorescent, electrospun fibers by doping fluorescent dye into polymer solution without altering fiber alignment
- Developed dual nozzle electrospray apparatus for polymer hybrid materials.

Introduction

In 2003, a National Academy of Sciences (NAS) report identified that several of the major stumbling blocks to the advent of practical fuel cells for application

to transportation were associated with the lack of appropriate materials for the fuel cell construction. Specifically, they rely too heavily on precious metals, including platinum, to be affordable. The PEM, a key part of a fuel cell, needed to function better at high temperatures and better dissipate the main byproduct: water. Finally, virtually everything in the fuel cell needed to be lighter. The core projects for this DOE sponsored Center at Michigan Tech have focused on several of the materials problems identified by the NAS. These include: new electrode materials, enhanced PEM materials, lighter and more effective bipolar plates, and improvement of the carbon used as a current carrier. Our research into these areas has been approached via seven different tasks.

Approach

This project will involve fundamental and applied research in the development and testing of lightweight and nanostructured materials to be used in fuel cell applications and for chemical synthesis. The advent of new classes of materials engineered at the nanometer level can produce materials that are lightweight and have unique physical and chemical properties. The grant will be used to obtain and improve the equipment infrastructure to support this research, and will also serve to fund seven research projects. These include:

- Development of lightweight, thermally conductive bipolar plates for improved thermal management in fuel cells;
- Exploration of pseudomorphic nanoscale overlayer bimetallic catalysts for fuel cells;
- Development of hybrid inorganic/organic polymer nanocomposites with improved ionic and electronic properties;
- Development of oriented polymeric materials for membrane applications;
- Preparation of a graphitic carbon foam current collectors;
- The development of lightweight carbon electrodes using graphitic carbon foams for battery and fuel cell applications; and
- Movement of water in fuel cell electrodes.

Results

Task 1 - Development of Lightweight, Thermally Conductive Bipolar Plates for Improved Thermal Management in Fuel Cells (King, Keith)

Composites containing varying amounts of a single filler along with combinations of different fillers were fabricated and tested. Results to date indicate that the compression molded composite containing 2.5 wt%

carbon black, 65 wt% synthetic graphite, and 6 wt% carbon nanotubes in polypropylene have an electrical conductivity of 91 S/cm and a thermal conductivity values of 6.6 W/mK (through-plane) and 24 W/mK (in-plane). These values are near the DOE conductivity targets of 100 S/cm and >20 W/mK.

Task 2 - Exploration of Pseudomorphic Nanoscale Overlayer Bimetallic Catalysts for Fuel Cells (Holles)

Ethylene and carbon monoxide adsorption studies to determine heats of adsorption for the Pd/Re samples and the Pt/Ni samples are ongoing. In addition, X-ray absorption spectroscopy studies were performed at the National Synchrotron Light Source at Brookhaven National Laboratory on the Pd/Re samples. Extended X-ray absorption fine structure (EXAFS) analysis will be performed on this data to determine interatomic distances and coordination numbers for the Pd. This will provide important evidence of the local geometric environment around the Pd. An extensive amount of effort was devoted to interpreting and analyzing the data obtained to date for all Pd/Re and Pt/Ni samples. The key result obtained from this analysis is shown in Figure 1.

This figure demonstrates the relationship between the ethylene hydrogenation turnover frequency and the measure hydrogen heat of adsorption. It is also known from first principles computational studies that the heat of hydrogen adsorption can be correlated with the center of d-band. Thus we can now correlate for the first time, the activity of a high surface area supported metal catalyst with a computationally predicted parameter. Based on Figure 1, ethylene hydrogenation activity could be further increased by synthesizing a Pd monolayer on gold (Pd_{ML}/Au) catalyst. Unfortunately, other studies indicate that in a PdAu system, Au will preferentially segregate on the surface.

FIGURE 1. This figure demonstrates the relationship between the ethylene hydrogenation turnover frequency and the measure hydrogen heat of adsorption.

Activities during the upcoming period will include continuing ethylene and carbon monoxide adsorption studies. In addition, samples will be synthesized with higher weight loadings to help make EXAFS characterization easier. EXAFS analysis of the current samples is ongoing.

Task 3 - Development of Hybrid Inorganic/Organic Polymer Nanocomposites (Mullins)

We made the particles using the newly purchased poly-L-lactic acid (PLLA, Grade 6202D) from NatureWorks, LLC. We purchased 6202D instead of 6200D, which was used in the first phase of the project, because the 6200D is no longer available. According to the manufacturer, 6202D is the best substitute for 6200D. In the lab, we used 1,2-dichloroethane as the organic solvent. The droplets formed were collected in a 200 mL distilled water-poly (vinyl) alcohol bath with magnetic stirring. The results for scanning electron microscopy (SEM) studied showed that the particles' size and distribution were huge and pores were formed on the particle's surface. The pores were mostly observed on the larger particles. The latter observation has never been found with the direct current voltage, which was used in the first phase of the project. This is a possibility due to the pulsed voltage applied. To solve this problem, we need to find a way to reduce the particles size. Currently, we are studying the effect of the pulse amplitude, polymer concentration, flow rate, and working distance on the pores. So far, it seems that reducing the flow rates might be the best option. At this point, effort will be taken to solve the problems before we study the effects of pulse width, pulse amplitude, and pulse frequency on the particle's shape, size, and size distribution systematically.

Task 4 - Development of Oriented Polymeric Materials for Membrane Applications (Gilbert)

One limitation of electrospinning aligned polymer fibers is the ability to control fiber diameter. In the current literature, most electrospun fibers, whether randomly oriented or uniaxially aligned, have great diameter variability. Our laboratory is developing methods of controlling fiber diameter toward making better anisotropic fiber/film materials.

With fixed primary working conditions, the polymer solvent was altered to obtain aligned PLLA fibers with three different fiber diameters. Thick polymer fibers were fabricated by electrospinning an 8 wt% polymer solution formed by dissolving PLLA in a mixture solvent (50/50 wt% of chloroform and dichloromethane). Electrospinning this polymer solution generated fibers with an average diameter of about 1.6 μm (Figure 2A). When using 1,1,1,3,3,3 hexafluoro-2-propanol (HFP) as the solvent, average fiber diameter was reduced to 800 nm (Figure 2B). By doping polymer solution with

FIGURE 2. Generation of PLLA fibers with varying diameter. (A) thick fibers; (B) intermediate fibers; (C) thin fibers. Images obtained at 3,500x. Scale bar = 10 μ m.

negatively charged species (BSA) at a concentration of 1 wt% with respect to mass of PLLA, the average fiber diameter was reduced to 300 nm (Figure 2C).

Task 5 - Preparation of Graphitic Carbon Foam Current Collectors (MTU: T. Rogers; Clemson University: O. Mefford)/Task 6 - Development of Lightweight Carbon Electrodes Using Graphitic Carbon Foams for Battery and Fuel Cell Applications (MTU: T. Rogers, B. Cornilsen, M. Chye, W. Yeo)

Under Area II, we have synthesized peroxyacetyl nitrate (PAN)-based carbon foams that can function as a mechanical support for electrochemically-active material (e.g., nickel hydroxide active mass) or catalytically-active metals. Because the carbon foam is

FIGURE 3. Swagelok Cell Connected to a Potentiostat for Cycling

graphitic, it is an excellent lightweight, porous current collector for a battery or fuel cell electrode. Our goals for carbon foams are to: (1) increase the macropore/mesopore space to hold more active electrode mass, and (2) increase the accessible micropore surface area so that a supercapacitor anode can be created. To test commercial foams and novel foams produced at Clemson University, we are examining the electrochemical performance of electrodes loaded with nickel hydroxide active mass by performing charge/discharge cycles in flooded and sealed cells (Figure 3). Significant progress has been made in optimizing active mass deposition in the working electrode of a nickel hydroxide battery cell as measured by efficiency of pore filling, accessibility to ion transport, and electrical contact with the carbon support. In a related application, we have conducted successful preliminary electrocatalysis experiments (hydrogen dissociation) on an alumina support as a prelude to future deposition of a bimetallic overlayer fuel cell anode catalyst on a carbon foam support. Such a catalyst may be able to reduce or replace the current use of platinum for the catalytically-active sites.

Task 7 - Movement of Water in Fuel Cell Electrodes (Allen)

Compression-Force Imaging and Measurements on GDL Samples

Use of the compression sample holder¹ during SEM imaging of fuel cell GDLs has shown that damage due to compression, as could be found in fuel cell stacks, is easily visible at very low magnifications. Figure 4a is an SEM image of a Mitsubishi MRC 105 with 9 wt% polytetrafluoroethylene after compression. Damage along the boundary of the compression ring and channel edges

¹ The unique compression sample holder was described in the last quarterly report.

FIGURE 4. (a) GDL after compression with channel. Channel imprint is visible indicating loss of conductivity along channel edges. Loss of conductivity due to internal damage which decreases the electrical conductance of the GDL. (b) GDL after compression without channel. Imprint of compression ring is visible indicating loss of conductivity along channel edges. Loss of conductivity due to internal damage which decreases the electrical conductance of the GDL.

can be seen. The channel edges are perpendicular to the edge of the compression ring. The material on the left edge is carbon paint which is used to secure the sample and ensure good conductivity for imaging. Damaged regions can easily be seen by the bright regions which indicate charge accumulation due to reduced electrical conductivity. Conductivity is decreased because of fiber separation or breakage. Figure 4b shows a second sample (Mitsubishi MRC 105) compressed without the channel in the compression ring. The internal damage to the GDL resulting from compression is not easily seen from optical inspection, but the reduced electrical conductivity clearly is visible from SEM imaging.

The sample holder developed for SEM imaging of GDL samples under compression can also be used to measure the stress-strain characteristics of GDLs. Two types of tests were performed: single thickness GDL samples and 20-sample GDL stacks. The single GDL sample compression tests (1, 2, 7, and 8) show

similar behavior. The 20-sample GDL stacks (tests 3-6) illustrate a greater stiffness than the single-thickness GDL sample.² The data is preliminary and further testing will be conducted.

Contact Angle Measurements on GDLs

The existing setup for contact angle measurements has been modified so as to facilitate the measurements at elevated temperatures while maintaining a high level of humidity. A second-level thermostat, has been assembled. This thermostat will be placed on the heated copper plate of the existing first-level thermostat. During the next quarter, the dependence of contact angle on temperature for various GDL samples will be studied.

Conclusions and Future Directions

The Center for Nanostructured and Lightweight Materials is funded until the end of December 2009. Additional key laboratory experiments are being conducted during the remainder of the year for all of the tasks above. Data collection and analysis should be completed by December 31, 2009.

- **Task 1:** Determine tensile and flexural properties of the carbon filled thermoplastic materials for fuel cell bipolar plates.
- **Task 2:** Activities during the upcoming period will include continuing hydrogen and carbon monoxide adsorption studies on the high weight loading Re sample. Once deposited, the overlayer materials will also be characterized using chemisorption.
- **Task 3:** The dual capillary electrospray apparatus will be used to produce core shell particles consisting of an interior liquid media and a polymer shell.
- **Task 4:** The electrospinning studies to control the diameter of polymer fibers will be concluded during the upcoming period.
- **Task 5:** During the summer, foam samples will be pyrolyzed and graphitized and sent to Dr. Rogers' laboratory at Michigan Tech for comparison to commercial foam materials in electrochemical service.
- **Task 6:** Future work will include varying the cut-off voltage, the nickel concentration in the deposition solution, and the pre-oxidation conditions and noting how these factors affect cycle life.
- **Task 7:** During the next quarter, additional stress-strain data will be collected for the GDL samples. A key issue to address is the role of surface friction

² The exception is test run 3 which is the initial compression of the 20-sample GDL stack. This test run exhibits a unique behavior associated with forcing the GDL samples into contact with one another.

between the GDL sample and the compression ring on the stress measurement. Contact angle measurements of water on GDL samples will be made for a range of temperatures up to 80°C.

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V.K.4 Martin County Hydrogen Fuel Cell Development*

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Contract Number: DE-FG36-08GO88107

Project Start Date: March 1, 2008
Project End Date: March 31, 2009

*Congressionally directed project

Technical Targets

- Power Output: 7-10 Watts (Unicell)

Approach

A low-cost, high-speed manufacturing process for microfiber fuel cells was transferred from a research and development level to a manufacturing environment. The microfiber manufacturing technology comprises an extrusion process in which all the components of a single fuel cell, i.e., the electrocatalyst of cathode and anode, the polymer electrolyte membrane, and the current collectors, are extruded into a single microfiber ranging in size from 400-1,000 microns (see Figure 1). To create a fuel cell “stack” these microfibers are bundled into a “Unicell” structure (see Figure 2).

Objectives

- Transfer extrusion manufacturing process from research and development to the manufacturing floor while maintaining performance and quality within anticipated specifications.
- Modify Unicell process equipment by fine tuning parameters to increase and optimize throughput while maintaining performance and quality within anticipated specifications.
- Reduction of balance-of-plant components to allow for lower cost fuel cell fabrication and simplified operation.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cell Manufacturing section (3.5.5) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) Lack of High-Volume Membrane Electrode Assembly (MEA) Processes
- (D) Manual Stack Assembly
- (E) Lack of Manufacturing Processes for Balance of Plant Components for PEM Fuel Cell Systems

FIGURE 1. Microfiber Fuel Cell

FIGURE 2. Unicell

Various parameters including production speed and product quality were analyzed to prove the viability of these processes at the manufacturing level.

Process equipment for extrusion of microfibrinous fuel cells was designed and constructed based on prior designs at the research and development level. This equipment was installed at a manufacturing facility and extruded cells were tested according to strict protocols. It was anticipated that these production runs would verify that extrusion line production can be reliably duplicated at the manufacturing level. For the next step in the process, Unicell production, the process equipment was evaluated and optimized to handle increased throughput while maintaining quality and performance. Research and development was conducted concerning the design and simplification of the fuel cell system (see Figure 3) for increased assembly speed. This was done by reducing the balance-of-plant components resulting in lower cost fabrication and simplified operation. Effects on quality and performance were evaluated.

FIGURE 3. Fuel Cell System

Accomplishments (see Figure 4)

- Extrusion manufacturing equipment designed and installed. Viability of extrusion process for continuous manufacturing confirmed.
- Unicell manufacturing equipment designed and installed. Viability of automated “stack” assembly confirmed.
- System design changes were identified which resulted in elimination of temperature controllers, valves and excessive humidification equipment resulting in significant system cost reductions and enhanced performance.

FY 2009 Publications/Presentations

1. A poster presentation was made at the DOE Annual Review (May 2009).

FIGURE 4. Performance Comparison between Research Facility and Manufacturing Plant

V.K.5 Fuel Cell Balance of Plant Reliability Testbed*

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Subcontractor:

Lockheed Martin-IDT, Akron, OH

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*Congressionally directed project

(D) Lack of Educated Trainers and Training Opportunities

Technical Targets

Reliability of the fuel cell system BOP components is a critical factor that needs to be addressed prior to fuel cells becoming fully commercialized. The goal of this project will be to develop a series of test beds that will test system components such as pumps, valves, sensors, fittings, etc., under operating conditions anticipated in real PEM fuel cell systems. Results will be made generally available to begin removing reliability as a roadblock to the growth of the PEM fuel cell industry.

Stark State College students participating in the project, in conjunction with their coursework, will gain technical knowledge and training in the handling and maintenance of hydrogen, fuel cells and system components as well as component failure modes and mechanisms. This fuel cell workforce development program will result in students trained in PEM fuel cell system technology.

The Technology Validation sub-program element does not develop new component technologies or sub-system configurations and, therefore, does not have technology targets. However, the components must support the fuel cell stack which has the following technical target for longevity:

TABLE 1. Progress toward Meeting Technical Targets for BOP Components for Transportation Applications

Characteristic	Units	2010/2015 Stack Targets	2009 Project Status
Durability with cycling At operating T $\leq 80^{\circ}\text{C}$	Hours	5,000	To be determined

Objectives

There are two primary objectives of this project:

- To establish a testing program resulting in a reliability database for candidate proton exchange membrane (PEM) fuel cell balance-of-plant (BOP) components; and
- To enhance the education of the technical workforce trained in PEM fuel cell system technology.

Technical Barriers

This project addresses the following technical barriers from the Technology Validation section (3.6) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan: Technology Validation:

- (A) Lack of Fuel Cell Vehicle Performance and Durability Data
- (D) Maintenance and Training Facilities

This project also addresses the following technical barriers from the Education section (3.9) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan: Education:

Accomplishments

- Students are being trained to the Hydrogen Safety Plan.
- Students have learned a greater depth of LabVIEW programming and are using a broader range of equipment and software programming techniques.
- Two of the test beds have been designed.
- Component assessments have been conducted.
- Test beds are in the process of being assembled.

Introduction

One of the major challenges that needs to be addressed by the fuel cell industry prior to full commercialization is the reliability of the components that comprise the complete system, particularly the BOP. As a potential developer and integrator of fuel cell systems, Stark State College of Technology's team member, Lockheed Martin, has identified BOP component reliability as a critical factor that needs to be addressed before fuel cell systems will be incorporated into aerospace platforms.

Approach

Stark State College and Lockheed Martin will develop a series of test beds that will test fuel cell system components such as pumps, valves, sensors, fittings, etc., operating under conditions anticipated in real PEM fuel cell systems. The test beds will operate continuously for months, or years, until a component fails. Parts that continue operating will have demonstrated lifetime for potential fuel cell systems. Parts that fail will be removed (the rest of the test bed restarted) and examined to learn why they failed. Feedback will be provided to manufacturers for product improvement. Results will be made generally available to begin removing reliability as a roadblock to the growth of the PEM fuel cell industry. A total of three test beds will be developed in this project – two at Stark State College and one at Lockheed Martin. Those at the College will be built and monitored by engineering technology students as part of their education program. A database of parts, operating conditions and lifetime data will be generated and updated regularly.

Results

A fuel cell system consists of a fuel cell and its supporting BOP – the pumps, valves, sensors, fittings, piping, etc. needed to turn a fuel cell into a useful power plant. Components in this complex system can have long-term exposure to hydrogen, air (oxygen), high purity water, heat and other chemicals. The BOP reliability test beds will be a simplified design, simulating the conditions of an operating fuel cell. The first two test beds are designed to replicate humidified hydrogen exposure in the PEM fuel cell at $\leq 80^{\circ}\text{C}$. These test beds are a hydraulic loop simulation of the fuel cell system to test the piping, connectors, sensors, valves, pumps, etc., without the fuel cell. Testing will be done to simulate the flow rates, temperature and pressure of operation, initially under a humidified nitrogen system with eventual operation under reactant conditions. This exposure would simulate the anode flow areas just before the fuel cell entrance and conditions in the hydrogen re-circulation loop. The humidified hydrogen would be circulated using a hydrogen blower such

as the Parker Hannifin Model 55™ Univane rotary compressor [1].

As required by DOE, a Hydrogen Safety Plan was prepared to address the issues of working with hydrogen. The greatest hazard is combustion from leaking hydrogen. A failure modes effects analysis of possible hazards leading to the accumulation of hydrogen and subsequent combustion was assessed for the test bed with the associated risk mitigation to limit or eliminate the components necessary to support a fire. All participants in the project are required to be trained in the safe use of hydrogen and compliance with the Hydrogen Safety Plan. Renovation of the project laboratory space at Stark State College has begun to comply with the safety standards.

Test bed component selection is also critical to safe operation with hydrogen. Electronic devices required one or more of the following: Factory Mutual compliance, intrinsically safe designation, compliance with Class I, Division 1, Group B operation or designated for hydrogen use. Stark State students have been selecting components and monitoring sensors for the operation of the test bed. All test bed equipment is commercial off-the-shelf, as components requiring non-recurring engineering costs or modification for fuel cell use were outside the scope of this project. Instruments were chosen for their compliance with materials and flow specifications. Students have been exposed to the various sensor instrumentation associated with fuel cells as well as the instrumentation and operation of fuel cells in the classroom.

Figure 1 shows the test bed process flow diagram. The test bed design can be viewed as two “separate” pieces. The upper flow diagram designated “Life Cycle Test” is the loop that will recirculate our humidified hydrogen. This loop will be pre-tested with nitrogen for leaks before hydrogen usage. Operating conditions will be 50 psi static, 80°C , 70-95% relative humidity and 6-7 SCFM flow rate in the closed-loop system. The lower loop is designated for dry nitrogen or air only. This consists of the blower platform and the dynamic response test system. This section is for the pre- and post-test validations in our reliability testing, pump performance mapping and pressure decay (leak) testing of the components.

Operation of the test bed requires participating students to have a greater depth of understanding in LabVIEW programming and exposure to a broader range of software programming techniques. The embedded controller requires LabVIEW programming and compiling to make a stand-alone program for data acquisition, control and analysis of the data. In addition, National Instruments DIADEM has been explored for its extra capability in data acquisition, data storage and analysis.

Testbed Design-Hydrogen Recycle

Test procedures are being developed to assess the reliability of the device under test.

Selection of the BOP components must be made on the basis that the materials chosen will affect the fuel cell lifetime. In the test bed assembly and testing procedures, care must be taken to minimize contaminants.

Finally, the test plan will take advantage of existing vendor reliability data to minimize testing time or sample size. By employing Weibayes Analysis (i.e., the zero failure method) on the component's previous history, vendor data can be leveraged to obtain confidence and reliability estimates without the time and expense of testing to failure, resulting in fewer samples being tested to a greater confidence level.

Safety protocols are in place at both Stark State College and Lockheed Martin locations to ensure the

safety of individuals working with and around the reliability test beds being created through this project. The first two BOP reliability test beds are in the process of being assembled and instrumented for reliability testing. This project continues as a cooperative program between industry and an educational institution for hands-on training of the PEM fuel cell workforce.

Future Work

- Student and subcontractor completion of test bed assembly and control logic.
- Operation of the test beds to obtain reliability data.
- Failure analysis of failed components.
- Construction and instrumentation of the third BOP reliability testbed in the coming academic year.

FY 2009 Publications/Presentations

1. *Fuel Cell Balance of Plant Reliability Testbed*, Vern Sproat, P.E., poster session at DOE Hydrogen Program Annual Merit Review, Washington, D.C., May 2009.

References

1. *Cost Analyses of Fuel Cell Stack/Systems*, J. Sinha, S. Lasher, and Y. Yang, DOE Hydrogen Program Annual Report, V.A.3.

V.K.6 Hydrogen Fuel Cell Development in Columbia (SC)*

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*Congressionally directed project

impedance responses and global performance, mechanistically, as a foundation for engineering durability during design and manufacture of fuel cells (Barriers A-G; Tasks 9-models, 10-long term failure mechanisms, 11-innovative fuel cell design and manufacture).

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section (3.4) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) Cost
- (B) Durability
- (C) Performance
- (D) Water Transport within the Stack
- (E) System Thermal and Water Management
- (F) Air Management
- (G) Start-up and Shut-down Time and Energy/Transient Operation

Objectives

- Development of metal-free oxygen reduction catalysts to reduce cost, facilitate manufacturing, and enhance durability of fuel cells (Barriers A-C; Task 2 electrodes).
- Development of redox stable mixed ionic and electronic conductors (MIECs) for bi-electrode supported cell (BSC) symmetrical solid oxide fuel cell (SOFC) designs, to reduce cost by simplifying manufacturing, enhance durability, and greatly reduce sensitivity to thermal cycling (Barriers A-C, G; Tasks 8-portable power, 11-innovative fuel cells, 10-long term failure mechanisms).
- Development of durable, low-cost seals for proton exchange membrane (PEM) stacks, through the establishment of laboratory characterization methodologies that relate to cell/stack performance (Barriers A, C; Task 6 Seals).
- Development of understandings and methodologies to establish hydrogen quality as it relates to PEM cell applications for transportation needs (Barriers B, C, G; Tasks 9-models for impurities, 8-portable operation).
- Development of a first principles multiphysics durability model based on interpretations of electrochemical impedance spectroscopy (EIS) data that link the multiphysics processes, the microstructure, and the material states, with cell

Technical Targets

Carbon-based catalysts: To develop non-precious-metal catalysts for PEM fuel cell with high selectivity and durability which perform as well as conventional Pt catalysts with a cost of at least 50% less than the target of 0.2 g (Pt loading)/peak kW.

SOFC materials: Develop SOFC electrode materials that enable direct operation on hydrocarbon fuels.

Carbon-based catalysts: Determine PEM seals materials that have no appreciable weight loss or leachants over a 60 week test period.

Hydrogen Contamination: Establish the rate and mechanism of NH_3 transport in PEM cells over a 60-week period; identify the species of sulfur contamination on Pt catalysts in the presence of various gas species, e.g., H_2O and O_2 .

Multiphysics based durability modeling: Use impedance spectroscopy to identify specific material state change driven degradation mechanisms during SOFC operation.

Accomplishments

- Metal-free oxygen reduction catalysts have been developed to reduce cost, facilitate manufacturing, and enhance durability of PEM fuel cells.

- Redox stable MIECs for BSC symmetrical (and other) SOFC designs have been developed.
- The development of durable, low-cost seals for PEM stacks, through the establishment of laboratory characterization methodologies that relate to cell/stack performance.
- Understandings and methodologies have been developed to enable the establishment of hydrogen quality as it relates to PEM cell applications for transportation needs.
- The development of first principles multiphysics durability models based on interpretations of EIS data that form a foundation for engineering durability during design and manufacture of fuel cells have been constructed for BSC SOFC designs.

Introduction

The activities of the present project are contributing to the goals and objectives of the Fuel Cells element of the Hydrogen, Fuel Cells and Infrastructure Technologies Program of the Department of Energy through five sub-projects. Three of these projects focus on PEM cells, addressing the creation of carbon-based metal-free catalysts, the development of durable seals, and an effort to understand contaminant adsorption/reaction/transport/performance relationships at low contaminant levels in PEM cells. Two projects address barriers in SOFCs; an effort to create a new symmetrical SOFC design with greatly increased durability, efficiency, and ease of manufacturing, and an effort to create a multiphysics engineering durability model based on EIS interpretations that associate the micro-details of how a fuel cell is made and their history of (individual) use with specific prognosis for long-term performance, resulting in attendant reductions in design, manufacturing, and maintenance costs and increases in reliability and durability.

Approach

- Work on a previous DOE project, DE-FC36-03GO13108, was leveraged to create new carbon-based, metal-free catalysts for oxygen reduction.
- Research under way in a partnership with NASA Glenn, Savannah River National Laboratory (SRNL) and ENrG Inc. is being leveraged to create a new symmetrical SOFC design with greatly increased durability, efficiency and ease of manufacturing.
- Recent advances at the University of South Carolina in controlled hydration and temperature characterization of polymer-based materials will be

used to establish a methodology for characterization of materials in seals in PEM stacks.

- On-going work with the National Renewable Energy Laboratory, Argonne National Laboratory, SRNL, and Los Alamos National Laboratory forms a foundation for the work on developing an understanding of the contaminant adsorption/reaction/transport/performance relationships at low contaminant levels in PEM cells.
- Conceptual foundations laid by research supported by the National Science Foundation and several industries including United Technologies Fuel Cells are being expanded to create a multiphysics engineering durability model based on EIS interpretations that associate the micro-details of how SOFCs are made and their history of individual use with long-term performance, to achieve reductions in design, manufacturing and operating costs.

Results

Only one example of salient results are presented in the limited space available here. Other results appear in the quarterly reports.

Mesoporous composite carbon-based metal-free catalysts are being developed under the direction of Prof. Popov. The goal of this project is to develop highly active and stable carbon-based metal-free catalysts and carbon composite catalysts with strong Lewis basicity (π electron delocalization) to facilitate the oxygen reduction reaction (ORR). New nitrogen-modified carbon composite catalyst was synthesized by pyrolyzing the cobalt- and iron-nitrogen chelate over a silicon dioxide (SiO_2) followed by a leaching and post-heat-treatment. The activity of the new catalysts were significantly enhanced which is attributed to the expected increase in the number of active sites. The stability optimization of the new catalysts is on going.

It was found that the presence of nitrogen, transition metal, and carbon is crucial to produce non-precious metal carbon-based catalysts for the ORR. The activity of these catalysts is promising; however, their stability is not comparable with the Pt counterpart. Typically, the catalyst performance significantly decreases as soon as fuel cell starts to operate despite the catalyst synthesis methods, membrane and electrode assembly (MEA) fabrication methods, and fuel cell operation conditions. In the present report, a new synthesis strategy was developed to increase the activity of the catalyst while maintaining its stability [1,2]. Figure 1 shows the polarization curves of PEM fuel cells using CC- SiO_2 and CC-Carbon catalysts, respectively. The cathode catalyst loadings are 2 mg cm^{-2} . The experiments were performed using 30 psi back pressure on both anode and the cathode. The CC- SiO_2 showed the current density

FIGURE 1. Current-voltage plot of PEM fuel cells using CC-SiO₂ and CC-Carbon catalysts at 75°C. The cathode catalyst loading was 2.0 mg cm⁻². The tests were run using H₂ and O₂ with back pressures of 30 psi/30 psi.

of 0.96 A cm⁻² at 0.4 V and 1.98 A cm⁻² at 0.2 V. The CC-Carbon showed the current density of 0.65 A cm⁻² at 0.4 V and 1.65 mA cm⁻² at 0.2 V. It is evident that the CC-SiO₂ showed higher catalytic performance than the CC-Carbon.

Conclusions and Future Directions

Future work includes the following tasks:

- Model the recovery of performance from contaminants such as sulfur.
- Improve the integrity of the carbon composite catalyst layer in the MEA.
- Measure the ionic conductivity of lanthanum strontium gallate magnesite pellets in different atmospheres and temperatures.
- Investigate compression set of seals for heating/cooling cycles; develop life prediction model.
- Complete button cell measurements to support EIS durability modeling.

Special Recognitions & Awards/Patents Issued

1. Prof. Ken Reifsnider, PI of this effort gave an invited keynote lecture at the ECS meeting in San Francisco in May, 2009.
2. The Crystal Flame Innovation Award in Research from FuelCell South was presented to Dr. Popov's research group for research work in the field of non-precious catalyst development and preparation thin film assemblies with nano-structured catalysts and the development of the pulse deposition technique for preparation of membrane electrode assemblies.

FY 2009 Publications/Presentations

1. Tan, J., Chao, Y.J., Wang, H., Van Zee, J.W., "Chemical and mechanical stability of EPDM in a PEM fuel cell environment," accepted for publication in *Polymer Degradation and Stability*, July 2009.
2. S. Park, B.N. Popov, Effect of cathode GDL characteristics on mass transport in PEM fuel cells, *Fuel* 88 (2009) 2068-2073.
3. N.P. Subramanian, X. Li, V. Nallathambi, S.P. Kumaraguru, H. Colon-Mercado, G. Wu, J.-W. Lee, B.N. Popov, Nitrogen-modified carbon-based catalysts for oxygen reduction reaction in PEM fuel cells", *J. Power Sources* 188 (2009) 28-44.
4. S. Park, B.N. Popov, "Effect of Hydrophobicity and Pore Geometry in Cathode GDL on PEM Fuel Cell Performance", *Electrochim. Acta* 54 (2009) 3473-3479.
5. H.-Y. Jung, S. Park, and B.N. Popov, "Electrochemical Studies of Unsupported PtIr Electrocatalyst as Bifunctional Oxygen Electrode in Unitized Regenerative Fuel Cell (URFC)", *J. Power Sources* 191 (2009) 357-361.
6. G. Liu, X. Li, B. N. Popov, "Stability Study of Carbon-Based Catalysts for Oxygen Reduction Reaction in Polymer Electrolyte Membrane Fuel Cells", *216th Meeting of the Electrochem. Soc.*, Vienna, Austria, October, 2009.

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1. G. Liu, B.N. Popov, "Development of non-precious oxygen reduction catalysts from N-doped ordered porous carbon", *Appl. Catal. B: Environ*, in revision.
2. X. Li, S. Park, B.N. Popov, "Highly stable Pt and PtPd hybrid catalysts supported on a nitrogen-modified carbon composite for fuel cell applications", *J. Power Sources* (in press).

VI. MANUFACTURING R&D

VI.0 Manufacturing R&D Sub-Program Overview

Introduction

The Manufacturing R&D Sub-Program supports research, development, and demonstration (RD&D) needed to reduce the manufacturing cost of fuel cell technologies and to develop a domestic supplier base. The Manufacturing R&D effort will enable the mass production of both supply and end-use technologies (in parallel with technology development) and will foster a strong domestic supplier capability. Activities will address the challenges of moving today's laboratory-produced technologies to high-volume, pre-commercial manufacturing to drive down the cost of fuel cell systems. Research will be conducted in coordination with the Department of Commerce and the White House Office of Science and Technology Policy's Interagency Working Groups. An RD&D technology roadmap has been developed with industry to identify critical technology development needs for high-volume manufacturing of high pressure storage and fuel cell systems.

In Fiscal Year 2009, manufacturing projects from a 2007 solicitation continued in the following areas: novel electrode deposition processes for membrane electrode assembly (MEA) fabrication, high-volume fuel cell leak-test processes, novel assembly processes for low cost MEAs, gas diffusion layer (GDL) cost reductions, and fabrication technologies for high-pressure composite storage tanks.

Goal

Research, develop and demonstrate technologies and processes that reduce the manufacturing cost of fuel cell and fuel storage systems.

Objectives

- Fuel Cells - Presently, fuel cell stacks are fabricated at low volume and the costs of these stacks is approximately \$3,000 per kW. This is 50 times the projected cost of \$60 per kW¹ for the same stack technology (2006) at high volume (500,000 units/year). The projected high-volume cost includes labor, materials, and capital expenditures, but does not account for manufacturing R&D investment. One objective of Manufacturing R&D is to enable this factor of 50 cost reduction in fuel cell stacks for stationary and transportation power systems.
- Hydrogen Storage - Another objective of Manufacturing R&D is to reduce the cost of making high-pressure carbon composite hydrogen storage tanks by a factor of 9 from 2005 costs.

FY 2009 Technology Status

This sub-program focuses on the manufacture of high pressure hydrogen storage and fuel cell technologies that will be needed in the early stages commercialization. Research investments are focused on reducing the cost of components currently used (or planned for use) in existing technologies, as well as reducing the cycle times of the processes being developed. Progress toward attaining the Manufacturing R&D objectives is measured in terms of the ability of funded research to reduce the cost of producing fuel cell technologies; and to increase manufacturing processing rates and annual manufacturing capacity.

The Multi-Year Research, Development and Demonstration Plan was updated in April 2007, with estimated status costs for fuel cell and hydrogen storage technologies. The current costs for these technologies are \$250/kWh–\$350/kWh for a 700 bar gaseous hydrogen storage system, and \$3,000/kW for polymer electrolyte membrane fuel cell stacks fabricated at low volume.

¹ 2006 TIAX estimate for 80-kW automotive fuel cell systems

FY 2009 Accomplishments

FY 2009 saw a number of advancements in manufacturing for fuel cells and quality assurance. UltraCell has analyzed fuel cell stack manufacturing methods, procedures, throughput times, labor times, yield, failure modes and investigated leak-test methods resulting in the creation of a specification for leak-testing. Ballard down-selected an on-line GDL coating weight measurement tool to demonstrate the means of achieving six sigma quality standards. W. L. Gore developed a model for evaluating decal lamination processes for high speed electrode deposition. An ultrasonic welding (electrodes to sub-gaskets) cycle time of less than one second was achieved by Rensselaer Polytechnic Institute, an improvement from the current process (heated press) cycle time of one minute. An on-line measuring process developed by the National Renewable Energy Laboratory validated the thickness of membranes manufactured by industry partners such as BASF and 3M.

Budget

The President's FY 2010 EERE Fuel Cell Technologies Manufacturing R&D budget request was zero to allow for focused efforts on more near-term technologies.

2010 Plans

Competitively awarded research projects will have reached a logical decision point in development.

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VI.1 Fuel Cell Membrane Electrode Assembly Manufacturing R&D

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- 3M, St. Paul, MN
- Arkema Inc., King of Prussia, PA
- Ballard Materials Products, Lowell, MA
- BASF Fuel Cells, Somerset, NJ
- Johnson Matthey Fuel Cells, West Chester, PA
- W.L. Gore and Associates, Elkton, MD

Project Start Date: July 16, 2007
Project End Date: September 30, 2013

Objectives

NREL and its collaborators are developing capabilities and knowledge related to in-line quality control that will assist manufacturers of polymer electrolyte membrane fuel cell (PEMFC) membrane electrode assembly (MEA) components (membranes, coated electrodes, and gas diffusion media) transition to high volume manufacturing methods. Our main tasks are:

- Evaluate and develop in-line diagnostics for MEA component quality control, and validate diagnostics in-line.
- Investigate the effects of MEA component manufacturing defects on MEA performance and durability.
- Further refine and validate models to predict the effects of local variations in MEA component properties.

These objectives have strong support from our industry partners. Our specific development activities have been and will continue to be fully informed by direct input from industry. As new technologies emerge,

and as the needs of the industry change, the directions of this project will be adjusted.

Technical Barriers

This project addresses the following technical barriers from the Manufacturing section (3.5) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) Lack of High-Volume Membrane Electrode Assembly (MEA) Processes
- (F) Low Levels of Quality Control and Inflexible Processes

Contribution to Achievement of DOE Manufacturing Milestones

This project is contributing to achievement of the following DOE milestones from the Manufacturing section (3.5) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- **Milestone 1:** Develop prototype sensors for quality control of MEA manufacturing. (4Q, 2011)
- **Milestone 2:** Develop continuous in-line measurement for MEA fabrication. (4Q, 2012)
- **Milestone 3:** Demonstrate sensors in pilot scale applications for manufacturing MEAs. (4Q, 2013)
- **Milestone 4:** Establish models to predict the effect of manufacturing variations on MEA performance. (4Q, 2013)

Accomplishments

NREL has accomplished the following:

- Established a diagnostic development platform based on an NREL-developed optical diagnostic system used in continuous photovoltaics manufacturing.
- Demonstrated two-dimensional (2D) membrane thickness measurement and defect imaging on membrane samples of different types and with different as-manufactured defects.
- Performed initial experiments indicating the potential to use the NREL-developed optical diagnostic to measure platinum in electrodes.
- Established test methodologies to quantify the effects of defects on MEA performance.

- Demonstrated the feasibility of using segmented-cell test equipment and methods to obtain spatially resolved information about the effects of defects.
- Used LBNL models to qualitatively explain key behaviors of MEAs with defects.
- Initiated collaboration with two of DOE's competitively awarded manufacturing research and development (R&D) projects, in accordance with our project charter.

Introduction

In Fiscal Years 2005-2007, NREL provided technical support to DOE in developing a new key program activity: Manufacturing R&D for hydrogen and fuel cell technologies. This work included a workshop on manufacturing R&D, which gathered inputs on technical challenges and barriers from the fuel cell industry, and subsequent development of a roadmap for manufacturing R&D. In late FY 2007, NREL initiated a project to assist the fuel cell industry in addressing these barriers, initially focusing on in-line quality control of MEA components. The project is relying on and utilizing the unique and well established capabilities of NREL's National Center for Photovoltaics for developing and transferring diagnostic and process technology to the manufacturing industry.

Defects in MEA components differ in type and extent depending on the fabrication process used. The effects of these defects also differ, depending on their size, location in the cell relative to the reactant flow-field, cell operating conditions, and which component contains the defect. Understanding the effects of these different kinds of defects is necessary to be able to specify and/or develop diagnostic systems with the accuracy and data acquisition/processing rates required for the speed and size scales of high-volume continuous manufacturing methods. Furthermore, predictive capabilities for manufacturers are critical to assist in the development of transfer functions and to enable assessment of the effects of material and process changes.

Approach

NREL and its partners are addressing the DOE Manufacturing milestones listed previously by evaluating, developing, and validating (in-line) diagnostics that will support the use of high volume manufacturing processes for the production of MEA component materials. Prioritization of this work is based on inputs from our industry partners on critical manufacturing quality control needs. We are focusing on diagnostic capabilities not addressed by

commercially available in-line systems. Understanding that specification of the required accuracy and precision of a diagnostic device to measure or identify material property variability or defects requires information about how this variability affects the functionality of the MEA. We are developing test methodologies to identify threshold values of size and/or extent of each important type of variability or defect. Threshold values are being elucidated by statistically designed experiments using MEA components with created defects, e.g., by laser or ion bombardment methods, of defined size or extent. These results will be validated by MEAs with components having actual as-manufactured defects of similar scale. Key behaviors identified by these tests are being modeled to provide additional understanding and, where modeling capabilities are lacking, additional refinement will be made so that predictive capabilities for the identified effects of defects are developed.

Results

A new diagnostic development platform, based on an NREL-developed optical instrument used in continuous manufacturing of photovoltaic cells, was established for fuel cell MEA component materials. Work in the past year using this platform led to the demonstration of 2D thickness imaging and defect identification on polymer electrolyte membranes of different types and with different as-manufactured defects. Figures 1 and 2 provide examples of this measurement on membrane samples with actual

FIGURE 1. 2-dimensional image of a PEMFC membrane sample measured with the NREL device (corresponding optical image in inset). The image shows bubble defects and a color shift in the sample. An area of ~3" by 3" is shown.

FIGURE 2. 2-dimensional image of membrane thickness showing “impression” defect in layer 1. The defect has an approximately 10% reduction in thickness. An area of ~3” by 3” is shown.

manufacturing defects. This capability represents an improvement over existing in-line measurement capabilities because it provides both imaging of defects and two-dimensional thickness measurement. As such, it provides the capability not only to represent the statistical variability of the membrane but to view, in real-time, actual defects. This could enable much more rapid diagnosis of the source of the defects and ultimately reduce scrap, improve reliability, and enhance customer satisfaction. Additional work with the new platform, as well with standard optical characterization data, showed that the NREL device may be useful in measuring many important MEA component properties. For example, initial experiments showed that electrode platinum content – a property deemed critically important for in-line measurement by our industry partners – can potentially be measured.

In parallel with our diagnostic development and evaluation work, we and our partners at the Colorado School of Mines and the University of Hawaii established test methodologies to quantify the effects of MEAs with defects compared to pristine MEAs. Consistent with our initial diagnostics focus on membrane thickness, we identified differential pressure (anode vs. cathode) single cell and segmented cell tests that enable comparative measurement of MEA

FIGURE 3. Open circuit voltage data from MEAs with non-Teflon[®] membranes under differential pressure (anode/cathode) test conditions. Membrane defects were ~1 mm in diameter.

FIGURE 4. Segmented cell performance data from MEAs with and without anode defect (62% reduction in thickness). The defect was located in segment 4 and resulted in a local loss of performance at higher current densities.

performance with membranes having thickness defects or pinholes. Figure 3 is exemplary of this work and shows a comparison of MEAs with membrane defects to a pristine MEA. The effects of electrode defects also were studied (see Figure 4), as well as gas diffusion layer defects relating to thickness, Teflon[®] content, and micro-porous layer voids. Of particular note in this aspect of our work is the demonstration of the feasibility of using segmented cell hardware and methods to obtain spatially resolved information on the local effects of defects within the MEA.

Conclusions and Future Directions

Conclusions

- Continued support and guidance from our industry partners is critical.
- The NREL-developed optical diagnostic can be used for imaging of membrane thickness and defects. Further development of this capability will be driven by industry needs.
- Segmented cell test hardware and methods can be used to obtain spatially resolved information about the local (within the MEA) effects of defects. Further work should be undertaken to optimize the design of the hardware.
- The LBNL MEA models provide qualitative understanding of the behaviors of MEAs with component defects.

Future Directions

- Install and commission the research web-line for in-line validation of diagnostic systems.
- Complete system-level development of selected diagnostics, based on industry partner needs, including configuring the system for wide-web use.
- Investigate the use of the NREL-developed optical diagnostic for measurement of prioritized material properties, including catalyst loading, porosity, and surface structure.
- Establish a library of performance and durability test methodologies to study the threshold values of priority defects, so that specifications for in-line diagnostics can be understood.
- Use our defect MEA testing results to validate current LBNL models and establish a predictive capability for the effects of as-manufactured defects.

FY 2009 Publications/Presentations

1. "A Study of the Relationships Between PEM Fuel Cell MEA Component Manufacturing Defects and Cell Performance and Durability," Williams et al., 2008 Fall ECS Meeting, Honolulu, HI.
2. "Utilization of a Segmented Cell to Detect Defects in Proton Exchange Membrane Fuel Cells," Bender et al., 2008 Fall ECS Meeting, Honolulu, HI.
3. "NREL MEA Manufacturing R&D Project," Ulsh et al., 2008 Fuel Cell Seminar and Exhibition, Phoenix, AZ.
4. "Gas-Crossover and Membrane-Pinhole Effects in Polymer-Electrolyte Fuel Cells," Weber, J. *Electrochem. Soc.*, 155, B521-B531 (2008).
5. "PEMFC MEA Manufacturing Quality Control R&D at NREL," Ulsh et al., 2009 National Hydrogen Association Conference and Hydrogen Expo, Columbia, SC.
6. DOE Hydrogen Program Annual Merit Review, oral presentation, May 2009.
7. "A Study of the Relationships Between PEM Fuel Cell MEA Component Manufacturing Defects and Cell Performance," Williams et al., 2009 Spring ECS Meeting, San Francisco, CA.

VI.2 Digital Fabrication of Catalyst Coated Membranes

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Project Start Date: June 1, 2007

Project End Date: March 31, 2009

Objectives

- Demonstrate basic process steps in digital fabrication of catalyst-coated membranes (CCMs) and membrane electrode assemblies (MEAs):
 - Ink formulation and delivery with industry standard print heads.
 - Catalyst layer quality and mechanical durability.
 - Electrochemical utility.
- Define advantages and disadvantages of digital fabrication:
 - Reduce large run MEA fabrication cost.
 - Versatile and agile process line.
 - Integration of new technology.
- Identify unique advantages of digitally fabricated CCM:
 - Z gradation in composition – pore, catalyst, ionomer distribution.
 - Variable catalyst loading in XY plane.

Technical Barriers

This project addresses the following technical barriers from the Manufacturing section (3.5) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) Lack of High-Volume Membrane Electrode Assembly (MEA) Processes
- (B) Manual Stack Assembly
- (F) Low Levels of Quality Control and Inflexible Processes

Contribution to Achievement of DOE Manufacturing Milestones

This project will contribute to achievement of the following DOE milestones from the Manufacturing R&D section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- M36** Select manufacturing technologies to be developed for producing electrolysis membrane assemblies. (2Q, 2008)
- M37** Develop specific technical targets for continuous fabrication of electrolysis membrane assemblies. (4Q, 2008)
- M39** Develop pilot scale, high-volume manufacturing processes for membrane assemblies. (4Q, 2010)
- M40** Demonstrate pilot scale, high-volume manufacturing processes for membrane assemblies. (4Q, 2012)

Accomplishments

- Demonstrated feasibility of digital fabrication by successfully fabricating and testing CCMs in single cells.
- Characterized CCM printing process including evaluation of substrate handling methods; characterization of print layer thickness, adhesion, uniformity; and demonstration of control of catalyst layer composition in Z and demonstrate fabrication of large area CCMs.
- Evaluated implications of digital fabrications (DF) on process line design and economics including comparison of processing methods, evaluation of process line throughput needs, and determination of means of integration with stack and system assembly steps and qualitative identification of potential process cost saving.

Introduction

The MEA and the CCM are at the heart of a proton exchange membrane (PEM) fuel cell. In large-scale automotive applications this component must be manufactured with minimal cost, high reliability and at speeds sufficient to match the fuel cell stack assembly process. In addition the automotive industry must “qualify” a production process as being able to meet the above criteria. Once qualification occurs it is substantially more difficult to adopt new fabrication

technologies and/or technical advances as they arise. In the short- to medium-term, it is cheaper to go with a known but potentially more expensive process than switch to a new process with many unknowns. Currently, the automotive industry is not committed to a particular MEA or CCM fabrication method and is actively exploring new methods that may have significant cost, quality or speed advantages.

This project has explored the initial feasibility of using printing technology (DF) to fabricate CCMs. Two key technical obstacles were 1) the formation of stable colloidal suspensions (inks) without large particle that could clog print heads and 2) the mechanical manipulation or handling of Nafion® membranes before, during and after the printing process. The CCMs were demonstrated to perform at least as well as commercially prepared membranes. However the primary advantage of DF is the ability to eliminate almost all pre- and post-deposition chemical washes and elimination of any hot press steps.

Approach

The approach of this project was to first demonstrate the feasibility of digital fabrication including ink development, demonstration of CCM printing and validation of electrochemical performance. This demonstrated the essential steps for DF of CCMs. In addition, the adhesion of the catalyst layer to the membrane was, in the as printed condition, impervious to all but rough scraping as well as long-term sonication in acid, methanol and water.

The next phase of the project was to evaluate the printing process with emphasis on controlling the swellability of Nafion® during printing, obtaining uniform catalyst layers of sufficient thickness and demonstrating the ability to control the composition in the Z and XY directions. It was also desirable to demonstrate printing on large membranes up to 500 cm².

Finally we qualitatively evaluated the implications of DF on process line design and economics and compared the DF process with the more conventional decal transfer process. Key were the simplification of the process line, the ability to meet throughput needs and integration of DF with stack and system assembly steps.

Results

Figure 1 shows the Z direction uniformity of an approximately 15 µm catalyst layer printed on a Nafion® membrane. The layer was uniform to much less than 1 µm over the sample examined. In the XY plane of the CCM, the catalyst layer was, under some circumstances, visibly irregular. Irregularity could be attributed to clogging of individual print jets and to too rapid of a printing speed for the volume of ink delivered.

FIGURE 1. Scanning electron micrograph of a DF catalyst layer (center of picture) on a Nafion® membrane (right of pictures). The scale bar is 20 µm.

Jet clogging is dependent upon ink composition, drying of ink at the jet orifice and the presence of humectants in the ink. Clogging was primarily a function of open air drying between prints. Most printers have a sealed docking station that prevents this drying. However the print facility that Hewlett-Packard designed for print protocol testing, did not have such a port and we were careful to not let the heads stand idle for more than approximately 10 minutes. We do not believe that jet clogging due to drying will present an ultimate technical barrier to printing CCM although on-line means of detecting jet function may be beneficial.

In addition, jets can readily clog if the ink colloid suspension has any number of particles of approximately the same size or larger than the jet orifice. Properly suspended solutions were essential and a procedure was devised that provided for an ink with a “shelf-life” of many days. Colloid stability is critical in printers, such as with inexpensive consumer printers, where the inks may sit unused for weeks if not months. In a large-scale industrial application, inks could be prepared on an as needed basis and used within a few hours or days of preparation. However, given the high cost of the ink as well as the membrane, jet clogging is an expensive failure mechanism and quality control of the ink during preparation and just prior to printing will be necessary.

Figure 2 shows a power curve for two CCMs with one prepared in our laboratory by printing techniques with 0.2 mg Pt/cm^2 and the other commercially purchased with 0.3 mg Pt/cm^2 . The DF-CCM was slightly better than the commercially prepared CCM. Given the substantially lower platinum content of the DF sample the performance difference is significant. In this case the CCM with lower catalyst loading gave better results. The peak power for these membranes was less than that reported in the literature under optimal operating conditions and less than reported by the commercial vendor for the membrane tested. We attribute the low power to test stand limitations and are working to improve the quality of our test stand.

Figure 3 is a photograph of a large CCM in the process of being printed. The objective in

FIGURE 2. Power curves for commercially available and digitally fabricated CCMs.

FIGURE 3. Photograph of the printer depositing catalyst layer over a 180 cm^2 area on a membrane with an exposed area of 320 cm^2 .

these experiments was to demonstrate that DF can accommodate the fabrication of large MEAs (up to 500 cm^2) as would be used by the automotive industry and also to understand how to manipulate the membrane before, during and after printing. After some experimentation with various clamping methods, we determined that, in ambient humidity, the membrane required solid physical clamping to maintain a flat substrate suitable for printing. An acrylic clamp was constructed and used to clamp damp Nafion® membrane. Seven mil thick membranes were able to withstand the tensile forces set up during drying in ambient humidity. Two mil membranes were however susceptible to tearing at the clamp edges. Ultimately a membrane 320 cm^2 was fixed in the clamp and was more than sufficiently flat to achieve good quality prints. No visible wrinkling occurred upon rewetting of the membrane either with sprayed on water or from water contained in the ink. However, the area of the printed catalyst layer (both sides) was limited to 180 cm^2 by the physical design of the print head which in this case prevented close approach to the clamp edges. From our examination of a wide variety of commercial print heads, most modern print heads will require less than about 5 mm of side clearance. In this work, the fixture used to hold the print head presented the greatest clearance problem. Design criteria for new membrane clamp and print head fixtures were developed from these results. By comparing print speeds of commercial high speed four color printers we estimated that approximately 20-30 printers would be required to print CCMs for 500,000 vehicles/year with 70 kW power plants. The critical and limiting step does not appear to be the actual printing step but the membrane handling process.

Conclusions and Future Directions

- DF simplifies the fabrication process by eliminating hot press or lamination steps and does not require chemical transformations. The catalyst layer exhibits strong adhesion to the membrane and cannot be removed by boiling in water and solvents and cannot be easily removed mechanically.
- DF is capable of printing large continuous areas with sufficient speed to meet or match stack assembly needs and can do so in an on-demand fashion without compromising quality or consistency.
- The electrochemical performance was comparable to commercial MEAs and given DF's ability to optimize the catalyst loading it may be possible to further improve performance or reduce catalyst loading.

FY 2009 Publications/Presentations

1. *Invention Report – Advantages of ink-jet printing for the fabrication of PEM fuel cell membrane electrode assemblies.* Inventors: Vish Vishwanathan, Silas Towne, Jim Holbery, Peter Rieke.
2. *Invention Report – Formulation of an ink for ink-jet printing of PEM fuel cell membrane electrode assemblies.* Inventors: Silas Towne, Vish Vishwanathan, Jim Holbery, Peter Rieke.
3. *Invention Report – In-situ 3D Mapping of Fuel Utilization, Gas Flow and Water Flooding in Manifolds and Gas Diffusion Layers of an Operating PEM Fuel Cell Using Hyperpolarized ^3He or ^{129}Xe Magnetic Resonance Imaging* Inventors: Kevin Minard Li-Qiong Wang, Paul Majors, Vish Vishwanathan, Silas Towne, Jim Holbery, Peter Rieke, Rick Jacob.

VI.3 Reduction in Fabrication Costs of Gas Diffusion Layers

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Subcontractors:

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- Ballard Power Systems, Burnaby, BC

Project Start Date: October 1, 2008

Project End Date: September 30, 2011

Program Multi-Year Research, Development and Demonstration Plan:

- (A) Lack of High-Volume Membrane Electrode Assembly Processes
- (F) Low Levels of Quality Control and Inflexible Processes

Contribution to Achievement of DOE Manufacturing Milestones

This project will contribute to achievement of the following DOE milestones from the Manufacturing R&D section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- **Milestone 1:** Develop prototype sensors for quality control of MEA manufacturing. (4Q, 2011)
- **Milestone 2:** Develop continuous in-line measurement for MEA fabrication. (4Q, 2012)
- **Milestone 3:** Demonstrate sensors in pilot scale applications for manufacturing MEAs. (4Q, 2013)

Accomplishments

- Completed the design feasibility and scalability analysis of the new process technologies.
- Completed multi-layer coating pilot trials:
 - Identified the major process elements for control and measurement.
 - Established design parameters for the coating module.
 - Ascertained process modifications required for integration into the current manufacturing line.
 - Determined design specifications for the coating ink delivery system.
- Completed in-line mixing lab-scale trials:
 - Established the major process variables for control and measurement.
 - Determined major design parameters for the in-line mixer.
 - Verified continuous liquid and solid feed material delivery requirements.
- Identified strategic in-line ink mixing and delivery process control and measurement tools and established their respective evaluation criteria:
 - Down-selected sensor technologies for capability demonstration of in-line ink viscosity measurement.

Objectives

- Reduce the fabrication costs of gas diffusion layer (GDL) products, and verify the design of a new production facility incorporating process technologies that meet automotive volume requirements at the DOE 2015 cost target.
- Demonstrate the means of achieving six sigma quality standards at high volume manufacturing.
- Develop and implement new, high volume GDL process technologies.
- Produce high performance GDLs for backup power fuel cells at lower cost in the near term.
- Research, develop, and implement new on-line process control and measurement tools consistent with high volume manufacturing.
- Advance the understanding of the relationships between process capabilities, GDL product properties, and fuel cell performance to direct process specifications that maximize production yields of high-performance, low-cost GDLs.

Technical Barriers

This project addresses the following technical barriers from the Manufacturing R&D section of the Hydrogen, Fuel Cells and Infrastructure Technologies

- Evaluated in-line particle size distribution technologies and completed lab-scale capability testing.
- Identified three continuous solids feeder technologies and performed capability testing.
- Evaluated feasibility of commercial in-line surface tension and bubble content technologies.
- Down-selected in-line substrate and GDL coating process control and measurement tools for assessment and development:
 - Collected first run, machine direction and cross-web scanning data using on-line coating weight tool.
 - Completed assessment of non-contact surface profilometry techniques and identified two candidate sensors potentially capable of in-line scanning substrate paper and coated GDL.
 - Established evaluation criteria and identified three systems for capability demonstration of on-line machine vision quality inspection, down-selecting one.
 - Established evaluation criteria and initiated assessment of in-line substrate and GDL thickness sensors.
- Assessed feasible techniques for on-line characterization of GDL chemical homogeneity and down-selected Raman and Fourier transform infrared (FTIR) spectroscopy for further research and development.
- Identified a high-resolution 3-dimensional (3D) imaging technique to provide information on the topology of the pore space and its changes during processing.
- Identified carbonization process parameters affecting final substrate paper morphology and requiring tighter control to reduce product variability.

Introduction

This project addresses the Manufacturing R&D subprogram's goal of research, development and demonstration of technologies and processes that reduce the manufacturing cost of proton exchange membrane fuel cell systems. Specifically, this project reduces the fabrication costs of high-performance GDL products, increases their manufacturing rate and demonstrates the means of achieving six sigma quality standards at high volume manufacturing.

In this first year, the team began development of new, high volume process technologies for integration into the existing GDL manufacturing line. Under

development are multilayer coating and in-line mixing and delivery processes. For the carbon paper substrate, introducing in-line mixing and delivery technology will increase carbon paper substrate product volumes and yields, and reduce raw material waste and product cost. For the GDL products, the incorporation of both multilayer coating and in-line mixing and delivery technologies will reduce the number of process steps, increase product volumes and yields, and reduce costs.

Research and development (R&D) of advanced in-line process control tools and measurement systems, consistent with high volume manufacturing, was also started. These tools are essential for ensuring product quality, integrating the new process technologies, decreasing overall scrap rates, and eliminating costly ex situ testing. To direct process specifications that reduce product variability, a study of the relationships between process capabilities, GDL product properties, and fuel cell performance was also initiated.

Approach

This project consists of three integrated technology development paths, conducted over a period of three years. Together, these technologies address the objective of high-quality, low-cost GDL roll goods near term, and form the foundation for verification of a new production facility incorporating new GDL manufacturing technologies that meet automotive volume requirements at the DOE 2015 cost target.

The primary path consists of the development and integration of new process technologies; specifically, multilayer coating and in-line mixing and delivery. The GDL manufacturing process at BMP is modular; thus, it is possible to replace effectively process components with improved equipment, add new functions, and add new technology. Initial multilayer coating and in-line mixing pilot trials are followed by process development on the manufacturing line. With manufacturing involvement on the development team, this approach ensures the manufacturability and compatibility of the new technologies, reduces the time to bring to full manufacturing capacity and provides for a seamless transfer of the technologies to production.

Key to the success of both new and existing GDL process technologies is that all of the process steps and support functions operate correctly in order to achieve high quality GDL products at low cost. On-line process control tools and measurement systems are critical to ensuring the process variables and product properties are on target. This project includes R&D of new in-line process control and measurement systems that are either: (1) required for the new process technologies; (2) required for improved process specifications to achieve six sigma or better quality standards; and/or (3) required for new control strategies arising from

continued development of our understanding of the relationships between process variables, GDL properties and fuel cell performance.

To date, the linkage of GDL ex situ properties to predict fuel cell performance is an on-going area of development for the fuel cell industry. Many customers still require fuel cell performance benchmark testing to establish the performance window of GDL products. Given this gap in property-performance understanding, introducing new process technology presents a challenge in ensuring all critical process variables are identified. Consequently, work will be undertaken to develop new process specifications and establish critical-to-quality and critical-to-performance characteristics. Fuel cell screening performance testing will be conducted in combination with the development of new ex situ material characterization techniques to link process variables with product microstructure, properties and performance.

Results

1. High-Volume, Low-Cost Process Technology Development

A design feasibility and scalability analysis of the new process technologies was completed in Fiscal Year 2009. Analysis benchmarks established by BMP included product specification requirements, performance, cost, quality, timing/delivery, flexibility, equipment and maintenance requirements, automation techniques, spatial layout, and waste minimization strategies. The criteria addressed strategic, organizational, and technological factors.

The design of essential equipment and systems for the new process technologies was completed in FY 2009. Design specifications for the multilayer coating equipment were established, followed by integration requirements for the coating module placement into the manufacturing line. Coating ink requirements by the coater were cascaded to the ink delivery system. In conjunction with the ink delivery system requirements, the in-line ink mixer specifications were established. Finally, the continuous liquid and solids feed-rates were specified from the in-line mixer raw material demand.

To establish the design requirements of the multilayer coater, coating module and ink delivery system, a pilot trial was conducted at the coating equipment manufacturer's laboratory. The major process elements that affect material variability and process accuracy were determined and translated into design specifications for the module integration, process variables requiring on-line control and measurement, and design specifications for the ink delivery system.

The basic solution coating parameters, and the need to combine drying process optimization with solution modification were established. The coating inks are non-Newtonian fluids thus the design of both the coater and ink delivery system must accommodate this behavior.

An evaluation of in-line mixing technology was completed in FY 2009. Important considerations for the evaluation of the mixer design included: incorporation and wetting out of powders, ink holdup, mixing shear rate range and control, bubble generation, and ink flow pulsation. Key selection criteria were the design of the mixing chamber and the speed and configuration of the mixing elements being easily modified to fine-tune the mixing process. The ability to modify the mixing setup is important for processing a variety of products, consistent with delivering flexibility to current GDL manufacturing practice. A pilot trial was performed in collaboration with an in-line mixer manufacturer. Basic process parameters were examined during the trial, and process variables requiring control and measurement were identified. Liquid and solids delivery requirements were established with consideration to the ink holdup/mixer residence time for variable production rates.

The evaluation of continuous solid feeders is continuing, with the design of the feeders driven by the properties of each solid raw material. These include volumetric and gravimetric screw, vibrating, rotary valve, belt, agitator, and disc feeders. Different delivery system configurations have been evaluated to reduce cost and improve efficiency. Physical and rheological properties of the liquid feed materials were measured under various temperatures and concentrations. Accurate, low shear, and pulse-less delivery of the liquid raw materials is directing equipment selection.

2. Development of In-line Process Control Tools and Measurement Systems

The selection of on-line process control and measurement tools and techniques for research and development was initiated in FY 2009. The tools selected were identified as being required to: ensure process variables and product properties of the new process technologies are on target; improve process specifications at high volume to achieve six sigma or better quality standards; reduce/eliminate costly ex situ characterization sampling and testing; and/or address new control strategies arising from continued development of our understanding of the relationships between process variables, GDL properties, and fuel cell performance. The primary selection requirement for commercial tool evaluation was their ability to be developed and adapted for high volume GDL manufacturing and to be verified and validated with known GDL ex situ test techniques.

A survey of measurement techniques that have the potential to characterize GDL homogeneity on-line was conducted. Early challenges for these techniques with respect to GDL materials characterization include: GDL surface roughness and subsequent errors in quantitative assignment, micro- versus macro-spatial resolution, bulk versus surface measurement characteristics, and interference/noise from other constituents in the substrate and sublayers not under detection. Raman and FTIR spectroscopy were selected as viable on-line techniques to measure the chemical composition of GDLs. Raman spectroscopy was capable of detecting poly-tetrafluoroethylene (PTFE) and carbon in the GDL while infrared (IR) spectroscopy was only capable of detecting PTFE. Figure 1 shows the spatial distribution of PTFE on the surface of a GDL obtained with Raman spectroscopy. Chemical mapping of carbon was possible through Raman spectroscopy but not through FTIR because of the absorbance of IR radiation by carbon. Both of these chemical surface-mapping techniques will be pursued because it is possible for FTIR spectroscopy to provide complementary information that Raman spectroscopy cannot. Specifically, water can be detected easily with FTIR but not with Raman.

Four classes of non-contact surface topography measurement techniques were evaluated for the on-line surface profile analysis of substrate paper and coated GDLs. The assessed techniques included confocal microscopy, interferometry, triangulation laser, and scattered light. A comprehensive review was conducted that examined the merits and limitations of the techniques. Capability testing of three down-selected instruments was initiated, with one sensor identified to date. The tool delivered International Organization for Standardization (ISO)-defined 2-dimensional

(2D) profiles, 3D surface topography, and 2D and 3D parameters in accordance with international standards using advanced ISO 16610 filtering techniques. Long run scan 2D profiles at scanning speeds representative of the web velocity were also demonstrated. Figure 2 exemplifies the measurement data received from this tool. A 2D roughness profile obtained by scanning the surface of a GDL is shown in 2(a). The ability to resolve a rough surface is shown in 2(b), the 3D surface topology of a substrate paper.

Evaluation and procurement of an on-line GDL coating weight measurement system was completed in FY 2009. The system was installed and first run coating weight data was collected down- and cross-web using the scanning sensors. Cross-web scanning at target web speed confirmed in-line measurement capability.

A key in-line product quality tool under development in FY 2009 was a machine vision inspection system capable of real-time monitoring of the coating processes. The system is expected to monitor line start-up and changeover, detect process upsets and catastrophic defects in-process, provide input signals for process control, and enable higher line speeds. Sets of representative defective samples were assembled and distributed to system manufacturers for capability testing and identification of system hardware configurations.

Assessment of commercial non-contact thickness sensors and moisture content tools continues. Thickness measurement methods that are under evaluation include: optical, single side laser triangulation, and dual laser triangulation. Available sensors will be tested on-line for robustness, resolution, accuracy, repeatability, range, and sampling speed. A potential moisture sensor technology employing near IR reflectance/transmittance

FIGURE 1. 2D spatial distribution of PTFE on the surface of a GDL, with lighter areas showing higher concentrations.

FIGURE 2. (a) Representative 2D roughness profile; and (b) 3D surface topology of rough substrate paper.

spectroscopy was identified. Due to the large amount of carbon in the materials, the resulting absorbance of IR radiation by carbon made it difficult to measure the moisture content accurately. Signal modifiers that have previously been used with carbon are being evaluated.

Particle size distribution measurement techniques utilizing laser light scattering, electrical sensing zone method, and ultrasonic spectroscopy (acoustic scattering) were evaluated. The difficulty in using a laser light scattering system was the need to dilute the inks, risk of particle agglomeration and potentially skewed distributions. Similarly, the electrical sensing zone method required the dilution of the inks and is subject to agglomeration. Ultrasonic spectroscopy, a new technology capable of analyzing concentrated multi-component mixtures in-line without the need for dilution, was selected for capability testing. The accuracy of the resulting size distributions was dependent upon the accuracy of the volume concentration of solids. Consequently, assessment of the particle size distribution accuracy will be evaluated in conjunction with the accuracy of ink solids content arising from the solids and liquid delivery and in-line mixing processes.

In-line viscosity measurement techniques under evaluation include rotational, falling piston, acoustic, and electromagnetic viscometers. The shear rates of the in-line sensors are generally constant; however, the shear rates in the coating processes are variable and the viscosity-shear rate relationship of the coating inks is non-linear. Although variable shear rate viscometers measure viscosities at the shear rates of interest over a wide range of temperatures, they are complex and not adaptable for in-line operation in this application. Consequently, variable shear rate instruments will be utilized for process development and fixed shear rate viscometers will be installed on-line, and the sensors strategically placed with a temperature control unit.

3. Development of GDL Process Parameter, Product Property, and Fuel Cell Performance Relationships

A substrate carbonization process study combining thermogravimetric analysis with lab-scale experiments and production plant trials was conducted in FY 2009 to investigate the influence of process steps on the final substrate carbon morphology, conditions for increasing thermo-oxidation/stabilization and carbonization line speeds, and to optimize current process conditions. Process parameters affecting the final substrate morphology were identified and procedural measures have been instituted to reduce product variability. During carbonization, the heating rate determines the evolution rate of volatiles, which affects the formation of pores. Lower heating rates are

preferable to produce small pores and increase carbon crystallinity. Higher heating rates may lead to formation of pinholes, cracks, blisters and distortions. In addition, higher gas flow rates increase pore size by facilitating removal of volatiles and preventing condensation/sooting reactions. To monitor the topology of the pore space and its changes during processing, high-resolution X-ray tomography (HRXRT) scanning was investigated. Figure 3 shows the results of the 3D imaging of P75 substrate containing PTFE. Figure 3(a) shows the raw image of a 2.51 μm HRXRT slice; and 3(b) is representative of the 3D reconstruction using an advanced visualization program. High-resolution permits the detection of small features required to correlate process parameters, pore structure characteristics and fuel cell performance. The development of quantitative processing steps to describe the porous structure, quantify PTFE and carbon in the solid phase, and introduce and quantify water distribution is continuing.

FIGURE 3. (a) HRXRT raw image slice of P75 substrate paper containing PTFE; and (b) Subsequent 3D reconstruction using advanced visualization program.

Conclusions and Future Directions

In FY 2009, this project launched three integrated technology development paths, namely (1) the development and integration of new, high volume process technologies; (2) the research and development of advanced in-line process control tools and measurement systems, consistent with high volume manufacturing; and (3) the development of process control strategies resulting from continued understanding of the relationships between process variables, GDL properties and fuel cell performance. In this first year of this project, the team:

- Completed multilayer coating and in-line mixing pilot trials, and established key design parameters for the equipment and process integration.
- Identified strategic in-line ink mixing and delivery process control and measurement tools, and established their respective evaluation criteria.
- Down-selected in-line substrate and GDL coating process control and measurement tools for assessment and development.
- Down-selected Raman and FTIR spectroscopy for further R&D of on-line characterization of GDL chemical homogeneity.
- Identified a high-resolution 3D imaging technique to provide information of the topology of the pore space during processing.
- Identified carbonization process parameters affecting final substrate paper morphology and requiring tighter control to reduce product variability.

In the next year, the future directions of this project include:

- Complete fabrication, installation and commissioning of new process technologies that include: multilayer coating module, coating ink delivery systems, in-line mixer and continuous solids and liquid delivery equipment.
- Complete evaluation, purchase, and on-line implementation of advanced process control tools and measurement systems that are under development.

- Complete substrate carbonization process study and introduce new process control procedures.
- Continue development of quantitative processing steps for HRXRT data to link GDL microstructure with material properties and fuel cell performance.
- Continue research and development of Raman and FTIR spectroscopy for on-line chemical homogeneity measurement of GDLs.
- Continue development of process variable, product property, and fuel cell performance relationships to direct new process specifications:
 - Build product process parameters-product properties relationships.
 - Conduct single cell fuel cell GDL screening performance testing.
 - Establish critical-to quality and critical-to-performance characteristics.

FY 2009 Publications/Presentations

DOE Hydrogen Program and Vehicle Technologies Program Annual Merit Review and Peer Evaluation Meeting, Washington, D.C., May 20, 2009.

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VI.4 Modular, High-Volume Fuel Cell Leak-Test Suite and Process

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Contract Number: DE-FG36-08GO18054

Subcontractors:

- Pacific Northwest National Laboratory (PNNL), Richland, WA
- Cincinnati Test Systems (CTS), Cleves, OH

Project Start Date: September 1, 2008

Project End Date: August 31, 2011

Objectives

- Design a modular, high-volume fuel cell leak-test suite capable of testing in excess of 100,000 fuel cell stacks per year (i.e., 50 fuel cell stacks per hour).
- Perform leak tests in-line during assembly and break-in steps.
- Demonstrate fuel cell stack yield rate greater than 95%.
- Reduce labor content to 6 minutes.
- Reduce fuel cell stack manufacturing cost by 80%.

Technical Barriers

This project addresses the following technical barriers from the Manufacturing section (3.5.5) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (F) Low Levels of Quality Control and Inflexible Processes

Contribution to Achievement of DOE Manufacturing Milestones

This project will contribute to achievement of the following DOE milestones from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- **Milestone 9:** Select stack assembly processes to be developed. (4Q, 2010)
- **Milestone 10:** Develop automated pilot scale stack assembly processes. (4Q, 2012)
- **Milestone 12:** Demonstrate pilot scale processes for assembling stacks. (4Q, 2013)

Accomplishments

- Completed analysis of fuel cell stack manufacturing processes. The analysis includes all manufacturing procedures, throughput time, labor time, yield, and failure modes.
- Completed the survey of mechanical properties of fuel cell stack components.
- Investigated and selected leak-test methods for the leak-test suite.
- Created specification for fuel cell leak-test suite lab prototype.
- Working on the design of leak-test suite lab prototype.

Introduction

There are three fluid circuits in a fuel cell stack. Any fluid leakage between these circuits or to the external atmosphere leads to reduced individual cell or stack performance and results in a failure during stack testing. Fuel cell stacks are typically hand assembled and tested, and it is very time-consuming. Furthermore, the leak-test equipment is often composed of expensive analytical devices, with extensive and excessive capabilities, that are not well suited to rapid testing of stack assemblies in medium- or high-volume manufacturing environments. High labor content and expensive test equipment limit the amount of online leak checks during the assembly process, leading to high scrap rates and low yields.

The development of a Modular, High-Volume Fuel Cell Leak-Test Suite and Process is proposed to address these challenges by reducing labor content; providing more robust, high confidence automated

testing; and increasing the speed and throughput at which manufacturing is performed. Each leak test component will be highly specialized to its specific task and optimized for high throughput, thereby allowing for dramatic cost savings. A variety of methods will be employed to test for leaks between the fuel cell fluidic paths and the environment during the entire process from build to break-in to final test. The test suite will enable manufacturers to select modular test components as needed.

Approach

Six leak-test methods were proposed in the project. These tests include crossover current, current interrupt, voltage decay, pressure decay, flexo-tiltometer test, and fuel cell sensor for coolant leak. These methods will be investigated, and some will be selected to implement in the leak-test suite. These tests will automatically perform in-line during fuel cell stack manufacturing. The leak-test methods not only check the overall leakage, but also identify the location of leak and accelerate the diagnostics and remediation of fuel cell stacks.

The phase I of the project focuses on the analysis of current manufacturing processes, stack failure modes, and leak-test processes. A variety of leak-test methods will be surveyed, and recommendations for the leak-test suite will be made. The leak-test suite prototype will be designed, fabricated, and evaluated. A leak-test suite with 50 stacks per hour capability will be designed. Phase II will focus on pilot production line modification, leak-test suite fabrication, integration, and verification. A limited production test run will be carried out to validate the 50 stacks per hour operation.

Results

We completed the analysis of stack manufacturing and assembly processes. Usually, stack manufacturing includes parts preparation, stack assembly, compression, leak test, break-in, performance test, and leak test after performance test. Qualified stacks are then integrated into fuel cell systems. All the steps are carried out manually, and the process is labor intensive and time-consuming. The throughput time (the elapsed time between parts entering and stack exiting the manufacturing process) is about several hours. The dominant factor is the break-in process, and reduction of break-in time has a huge impact on the final design of leak test suite, especially flexo-tiltometer. Typical break-in time for a phosphoric acid/polybenzimidazole membrane electrode assembly (MEA) is 16–24 hours. By MEA pretreatment and conditions optimization, UltraCell is able to reduce the break-in time to several hours. The cell voltage reaches more than 95% of the maximum performance in a short period of time after

the beginning of the break-in process. The yield of the stack build is not stable, and it highly depends on the quality of incoming parts, especially the MEA, and the skills and experience of the stack builders. There is a great opportunity to improve the stack yield. Several stack failure modes during manufacturing have been identified. Initial work was focused on developing linkages between common stack failure modes and the underlying root causes. Methods for screening these root causes out earlier in the manufacturing process, through incoming material control and in-line measurement, will then be developed. To this end, PNNL and UltraCell have begun review and analysis of the stack build history in an effort to better understand the various failure modes, their root causes, and the component and process parameters which contribute. The inspection data of bipolar plate (thickness, socket depth, flow channel depth, and flatness) were collected. The dimensional variation of stack components was analyzed to determine whether it is a major source of stack failure.

A variety of fuel cell components, provided to PNNL by UltraCell, were surveyed using dynamic mechanical analysis. The first objective was to ensure that quality data could be obtained on the instrument available and to understand this particular instrument's limits. Secondly we wished to examine various dynamic mechanical tests and begin to understand which would be most useful in a plant assembly line. Third, we wished to qualitatively understand the basic mechanical properties of each component. All tests so far were conducted in a compression mode. The following tests were used for this round of experiments: static stress scan, creep and recovery, frequency scan, and dynamic temperature scan. Compressive Young's modulus of individual fuel cell stack component can be obtained from the static stress scan test. The creep of stack components under constant load can be obtained from the creep and recovery test. The frequency scan and dynamic temperature scan are not very informative for some gaskets due to the small thickness. The static stress and creep and recovery tests are very important for the selection of materials with better sealing properties. The test results also help us better understand the stack behavior during manufacturing and operation, identify the root causes of fuel cell stack leakage, and reduce the stack failures.

Several leak-test methods were investigated. They are the crossover current test, current interrupt test, voltage decay test, and pressure decay test. In summary, the crossover current test, current interrupt test, and voltage decay test can be used to detect crossover leak in fuel cell stacks. All three methods are capable of pinpointing the location of crossover leaks. However, the current interrupt test is not very sensitive, and it does not meet the detection limit required for fuel cell stacks. Both the crossover current test and voltage decay test

have good sensitivity and are easy to implement. These two methods and the pressure decay test will be included in the fuel cell stack leak-test suite and laboratory prototype. Some results of these tests are shown in Figures 1, 2, and 3.

UltraCell, PNNL, and CTS worked together to develop a specification for the leak-test suite laboratory prototype. The flowchart of the test suite is shown in Figure 4. The specification includes required functions, detail procedures to perform these functions, hardware, software, graphical user interface, gas interface, electrical interface, heating system, and compression stand. CTS is currently working on the mechanical design of the fuel cell test fixture. This fixture is comprised of components which will:

FIGURE 1. Crossover Current Test (fuel cell with crossover leak shows high crossover current)

FIGURE 2. Open Circuit Voltage (OCV) Decay Test (fuel cell with crossover leak shows low OCV and high decay when hydrogen is pressurized)

FIGURE 3. Pressure Decay Test (fuel cell with leak show high pressure decay)

FIGURE 4. Leak-Test Suite and Processes

- Accurately locate and maintain the fuel cell in the fixture.
- Provide sealing mechanisms to provide leak-free connections between the fuel cell and the leak test equipment.
- Provide a means of accurately applying static and dynamic compression force to the fuel cell stack.
- Provide mounting locations for height sensors to measure fuel cell compression.
- Provide for location and application of an electrical interface to monitor the fuel cell performance.
- Provide for heating/cooling and temperature monitor of the fuel cell assembly.
- Provide a means to torque tie bolts while the stack is compressed in the fixture.
- Provide change tooling as necessary to support testing of fuel cell stacks with different number of cells.

Conceptual design of the sealing mechanism for the gas ports has been completed. Work is continuing in the design of the electrical connectors, as well as the part fixture and heating components. CTS is currently working on the specification of the control, electrical, pneumatic, and hydraulic hardware for testing of the fuel cell stack assembly. As the specification for the flexo-tiltometer forces and frequency are refined and confirmed, a hydraulic package will be selected and quoted.

Conclusions and Future Directions

The conclusions include the following:

- Completed the analysis of fuel cell stack manufacturing processes. The stack break-in process is a dominant factor determining the throughput time, and has a significant impact on the leak-test suite design. Several failure modes have been identified. There is room to improve the stack yield.
- Investigated and selected leak-test methods for leak-test suite. Crossover current, open circuit voltage decay, and pressure decay will be included in the leak-test suite.
- Investigated fuel cell stack components. Dynamic mechanical analysis is an excellent method to study mechanical properties and behavior of a fuel cell stack and its components.
- Created specification for leak-test suite lab prototype. Detail procedures have been written.
- Started design leak-test suite lab prototype.

Future directions include the following:

- Design and fabricate leak-test suite lab prototype with 5 parts per hour capacity.
- Test leak-test suite lab prototype and generate stack quality metrics.
- Design leak-test suite with 50 parts per hour capacity.

FY 2009 Publications/Presentations

1. Kaye, I. et al., "Modular, High-Volume Fuel Cell Leak-Test Suite and Process", presentation at the 2009 Hydrogen Program and Vehicle Technologies Program Annual Merit Review and Peer Evaluation Meeting, Arlington, Virginia, May 18–22, 2009.

VI.5 Manufacturing of Low-Cost, Durable Membrane Electrode Assemblies Engineered for Rapid Conditioning

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Contract Number: DE-FC36-086018052

Subcontractors:

- UTC Power, South Windsor, CT
- University of Delaware, Newark, DE

Project Start Date: October 1, 2008

Project End Date: December 30, 2009

Objectives

The overall objective of this project is to develop unique, high-volume manufacturing processes that will produce low-cost, durable, high-power density 3-layer membrane electrode assemblies (MEAs) that require little or no stack conditioning:

- Manufacturing process scalable to fuel cell industry MEA volumes of at least 500k systems/year.
- Manufacturing process consistent with achieving \$15/kW_e DOE 2015 transportation stack cost target.
- The product made in the manufacturing process should be at least as durable as the MEA made in the current process for relevant automotive duty cycling test protocols.
- The product developed using the new process must demonstrate power density greater or equal to that of the MEA made by the current process for relevant automotive operating conditions.
- Product form is a 3-layer MEA roll-good (anode electrode + membrane + cathode electrode).
- The stack break-in time should be reduced by at least 50% compared to the product made in today's process, and break-in strategies employed must be consistent with cost targets.

For contractual reasons, this project has been split into two phases. The scope of this report is limited to Phase 1.

Phase 1 Objectives

- Characterize current commercial MEA performance:
 - Utilize advanced test protocols to understand gaps between current MEA performance and DOE targets.
 - Obtain data to enable future comparison with MEAs made by new processes.
- Develop a high-volume cost model for the current commercial MEA and estimate potential savings:
 - Understand gaps between current process costs and DOE targets.
 - Obtain baseline data to enable future comparison with new processes.
 - Estimate potential savings to justify kick-off of new process development (Go/No-Go decision).
- Develop a non-linear multi-layer mechanical model:
 - Develop a deeper understanding of failure mechanisms of the current MEA.
 - Use model to optimize properties of the MEA that will be made in the new low-cost process.
- Develop an MEA conditioning model:
 - Develop a deeper understanding of conditioning mechanisms of the current MEA and conditioning protocol.
 - Use model to optimize:
 - Properties of the MEA that will be made in the new low-cost process which affect conditioning.
 - Conditioning protocol (in situ stack protocol and/or ex situ MEA protocol) for the MEA that will be made in the new low-cost process.

Technical Barriers

This project addresses the following technical barriers from the Manufacturing section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) Lack of High-Volume Membrane Electrode Assembly (MEA) Processes
- (D) Manual Stack Assembly

Contribution to Achievement of DOE Manufacturing/ Fuel Cells Milestones

This project will contribute to achievement of the following DOE milestones from the Manufacturing and Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

3.5 Manufacturing R&D/ Fuel Cells/ Task 1: Membrane and MEA

4	Establish models to predict the effect of manufacturing variations on MEA performance. (4Q, 2013)
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3.4 Fuel Cells/ Task 3: Membrane Electrode Assemblies Meeting All Targets

38	Evaluate progress toward 2015 targets. (4Q, 2012)
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Accomplishments

- Characterization (power density, conditioning, mechanical durability, chemical durability) of current commercial MEA performance is complete. Gore's MEAs exceeded 2,000 hours of accelerated mechanical durability testing, which has been equated to achieving 9,000 hours of membrane durability in an 80°C automotive duty cycle. This exceeds the DOE 2015 membrane durability target of 5,000 hours.
- Cost modeling of the current commercial MEA process is complete. The model results indicate that a 17% reduction in the cost of the high-volume base case 3-layer MEA is attainable, given the potential process improvements that will be explored in Phase 2.
- A quasi-static elastic/plastic layered structure MEA mechanical model has been modified to include visco-elastic/plastic behavior and data collection to calculate model input parameters has begun. The model will be used to predict MEA lifetimes for a variety of temperature and relative humidity cycling scenarios.

Introduction

Over the past 20 years, great technical progress has been made in the area of improving power density and durability of fuel cell stacks, so much so that most

of the requisite technical targets are now within reach. Yet, three major technical challenges remain. First and foremost is meeting the cost targets. The second challenge is producing components that are amenable for use in a high-speed, automotive assembly line. One impediment to this latter goal is that stack components must currently go through a long and tedious conditioning procedure before they produce optimal power. This so-called "break-in" can take many hours, and can involve quite complex voltage, temperature and/or pressure steps. These break-in procedures must be simplified and the time required reduced, if fuel cells are to become a viable power source. The third challenge is to achieve the durability targets in real-world operation. This project addresses all three challenges: cost, break-in time, and durability for MEAs of fuel cell stacks.

Approach

The overall objective of this project is to develop unique, high-volume manufacturing processes for low-cost, durable, high-power density 3-layer MEAs that require little or no stack conditioning. In order to reduce MEA and stack costs, a new process will be engineered to reduce the cost of intermediate backer materials, reduce the number and cost of coating passes, improve safety and reduce process cost by minimizing solvent use, and reduce required conditioning time and costs. MEA mechanical durability will be studied and optimized using a combination of ex situ mechanical property testing, non-linear mechanical model optimization, and in situ accelerated mechanical durability testing. Unique enabling technologies that will be employed in new process development include:

- Direct coating which will be used to form at least one membrane-electrode interface.
- Gore's advanced expanded polytetrafluoroethylene membrane reinforcement and advanced perfluorosulfonic acid ionomers which enable durable high-performance MEAs.
- Advanced fuel cell testing and diagnostics.

Results

Characterization (power density, conditioning, mechanical durability, chemical durability) of the current commercial MEA performance is complete.

- MEA power density was characterized in fuel cell performance tests that were designed to be relevant to a variety of fuel cell applications (see Figure 1). Polarization curves were generated using the following operating conditions:

FIGURE 1. Power Density Characterization of the MEA Made in the Current Commercial Process

Condition	Description	Tcell (°C)	Inlet RH (Anode/Cathode)	Stoich (Anode/Cathode)	Pressure (psig)
1	Stationary	80	100/100%	1.3 H ₂ /2.0 Air	0
2	Wet	70	152/152%	1.3 H ₂ /2.0 Air	0
3	Current Auto	80	33/33%	1.3 H ₂ /2.0 Air	7
4	Future Auto	95	19/19%	1.3 H ₂ /2.0 Air	7

RH – relative humidity

- Break-in was characterized using the following protocol. Gore's current commercial MEAs achieved break-in within 2 hours of cycling.

Tcell (°C)	Pressure (psig)	Inlet RH (Anode/Cathode)	Stoich (Anode/Cathode)
80	25	100/100%	1.2 H ₂ /2.0 Air

Step cycle between 0.6V, open-circuit voltage (OCV), 0.3 V, OCV, 0.6 V, OCV, etc. for 2 hours.

- Replicate MEAs from Gore exceeded 2,000 hours of single-cell accelerated mechanical durability testing using the cycle given below, which has been equated to achieving 9,000 hours of membrane durability in an 80°C automotive duty cycle. This result exceeds the DOE 2015 membrane durability target of 5,000 hours.

Tcell (°C)	Pressure (kPa)	Flow (Anode/Cathode, cc/min)
80	270	500 N ₂ /1,000 N ₂

Cycle between dry feed gas and humidified feed gas

(sparger bottle temp = 94°C)

Dry feed gas hold time: 15 seconds

Humidified feed gas hold time: 5 seconds

For further protocol information, see: W. Liu, M. Crum, ECS Transactions 3, 531-540 (2007).

- Chemical durability was characterized using the protocol given below. After 300 hours of testing, replicate Gore MEAs maintained low degradation as evidenced by fluoride release rates under 5.45E-08 g F/hr cm².

Tcell (°C)	I (mA cm²)	Inlet RH (Anode/Cathode)	Pressure (kPa)	Flow (Anode/Cathode, cc/min)
95	0	50/50%	270	100/200 cc/min

For further protocol information, see: W. Liu, M. Crum, ECS Transactions 3, 541-550 (2007).

Cost modeling of the current commercial MEA process has been completed.

- Model results indicate that a 17% reduction in the cost of the high-volume base case 3-layer MEA is attainable given the potential process improvements that will be explored in Phase 2. See Figure 2

Process Waste Map

Membrane Coating		
Process Costs	Primary forms of waste	Modeled Process Improvements
Ionomer solution	line losses, edge trim, membrane thickness	Membrane thickness reduction
ePTFE	edge trim, thread-up	
Backers	all backers	Reusable backer
Solvent/disposables	all	
Process/MOH	time	
DL	time	
Other		
Electrode Coating		
Process Costs	Primary forms of waste	Modeled Process Improvements
Catalyst	line losses, edge trim, electrode residuals	Reduce scrap with better coating process
Backers	all backers	No backers
Solvent/disposables	all	
Process/MOH	time	
DL	time	
Other		
3 Layer Roll-Good Finishing Operations		
Process Costs	Primary forms of waste	Modeled Process Improvements
Electrodes	edge trim	Eliminate this process
Membrane	edge trim	Eliminate this process
Process/MOH	time	Eliminate this process
DL	time	Eliminate this process
These were included in the improved process cost model		

FIGURE 2. 3-Layer MEA Manufacturing Process Waste Map

for process waste map and key improved process assumptions.

Possible paths for establishing time-dependent mechanical properties were investigated.

- Methods to characterize ionomer membrane visco-elastic and visco-plastic properties were investigated using a TMA (thermal mechanical analyzer) modified for humidity control. As a pilot investigation, small samples (1/8" diameter discs) of NAFION^{®1} 112 membrane were mounted onto the custom-built stage equilibrated within the test chamber at selected temperature humidity combinations (25°C and 30% RH; 50% and 90% RH). A 0.01 Newton preload was applied to hold the specimen flat on the loading stage while allowing 30 minutes for the sample and chamber to equilibrate. The sample was then loaded compressively with a 1 Newton load (corresponding to 0.125 MPa pressure) and held for 15 minutes before releasing the load. During this loading, three distinct phases of deformation were observed. During the application of the compressive load, the specimen thickness decreased rapidly, corresponding to an elastic stress-strain response. As the load was held, the specimen continued to compress, indicating a creep response. When the load was released, the specimen slowly began to regain thickness in a recovery response. For these pilot investigations, the load cycle was held constant. Full equilibrium and recovery were not realized at any stage in the test. Consequently, in

future studies, an optimum load-time cycle will be established and used to collect the relevant time-dependent data.

Existing numerical model was extended to include time-dependent (visco-elastic/plastic) properties.

- The applicability of ABAQUS finite element modeling was investigated for simulating the time-dependent response of ionomer membrane by constructing a small axisymmetric model. Data were from a previous study in which the University of Delaware conducted a preliminary investigation of time-dependent properties of NAFION[®] 112 membrane in a water environment. In the model, a load sequence corresponding to the sequence used in the experimental investigation (load-hold at constant displacement) was applied. The time-dependent deformation was calculated for this load sequence and compared to the experimental results (see Figure 3). The results show that a simple Maxwell model with nonlinear strain is adequate to capture the experimental response. This material model will be implemented in numerical simulations of stresses in fuel cell operation.

Various changes in the conditioning model were made to simulate the conditioning mechanism.

- Expression for oxygen reduction reaction kinetics was modified to capture the effect of available active area and to allow incorporation of the effects of certain contaminants.
- A two-step approach has been adopted for the model validation with the baseline of Gore's MEA conditioning experimental data:

¹ NAFION is a registered trademark of E. I. DuPont de Nemours company.

FIGURE 3. (a) Experiment conducted via loading and hold at constant strain. Markers indicate experimental values; solid black line indicates the deformation using a Maxwell model for viscoelastic response. (b) Using the extracted material parameters for the Maxwell model, the graphs show the predicted response for a case of loading followed by holding at constant force.

- Polarization curve of a conditioned cell will be used to fit the model results. This step will ensure that the model is using correct property values for the baseline MEA and is in quantitative agreement with the experimental results.
- Intermediate polarization curves collected throughout the conditioning protocol will be used to fit the model. At the end of the second step, the model will be fully validated with baseline MEA conditioning data.
- Preliminary results of validation analysis are shown in Figure 4. Using sensitivity analysis and resistance information from experiments, ionomer ionic conductivity and available catalyst area (A_s) were tuned to match the model results with the experimental data. Figure 4 clearly shows excellent

FIGURE 4. Preliminary results for model validation. Experimental data corresponds to the polarization curve for historic stationary (HS) operating condition ($T_{\text{cell}} = 80^\circ\text{C}$, anode/cathode $T_i = 80^\circ\text{C}$, anode/cathode stoichiometry = 1.3/2.5) for a fully conditioned cell.

agreement between the model and experimental data in the activation and ohmic regions. However, there is a disagreement in the mass transport limitation ($I > 1 \text{ A/cm}^2$). An investigation to identify the causes of disagreement between model results and experimental data at higher current density is underway. Potential causes could be inappropriate capillary pressure relationship and/or diffusion media/catalyst layer water transport properties.

Conclusions and Future Directions

The combination of Gore's advanced materials, expertise in MEA manufacturing, and fuel cell testing with the mechanical modeling experience of the University of Delaware and the fuel cell modeling experience of UTC Power, enables a robust approach to development of a new low-cost MEA manufacturing process.

- A quasi-static elastic/plastic layered structure MEA mechanical model has been modified to include visco-elastic/plastic behavior and data collection to calculate model input parameters has begun. When data collection is complete, the model will be validated with MEA durability testing and then used to predict degradation for different MEA constructions in a variety of temperature and relative humidity cycling scenarios.
- Further modifications of a MEA performance model, which includes conditioning phenomena, will be made in order to better represent break-in and peak performance. The model will be validated with experiments and exercised to explore the effects of MEA processing and in situ conditioning protocols on conditioning time.
- MEA cost model results indicate that a 17% reduction in the cost of the high-volume base case 3-Layer MEA is attainable given the potential process improvements that will be explored in

Phase 2. Laboratory-scale equipment which has the potential to achieve the MEA process cost reductions determined by the cost model will be specified, procured, and qualified in preparation for prototype process development in Phase 2.

FY 2009 Publications/Presentations

1. 2009 Hydrogen Program Annual Merit Review: mf_04_busby.

VI.6 Adaptive Process Controls and Ultrasonics for High Temperature PEM MEA Manufacture

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Subcontractor:
Arizona State University, Tempe, AZ

Project Start Date: September 1, 2008
Project End Date: February 28, 2012

Objectives

The high level objective of the proposed work is to enable cost-effective, high-volume manufacture of high-temperature proton exchange membrane (PEM) membrane electrode assemblies (MEAs) by:

- achieving greater uniformity and performance of high-temperature MEAs by the application of adaptive process controls (APC) combined with effective in situ property sensing to the MEA pressing process; and
- greatly reducing MEA pressing cycle time through the development of novel, robust ultrasonic bonding processes for high-temperature (160-180°C) PEM MEAs.

Technical Barriers

This project addresses the following technical barriers from the Manufacturing section (3.5.5) of the Hydrogen, Fuel Cells and Infrastructure Technologies (HFCIT) Program Multi-Year Research, Development and Demonstration Plan:

- (A) Lack of High-Volume Membrane Electrode Assembly (MEA) Processes

- (F) Low Levels of Quality Control and Inflexible Processes

Contribution to Achievement of DOE Manufacturing Milestones

This project will contribute to achievement of the following DOE milestones from the Fuel Cell Manufacturing section of the HFCIT Program Multi-Year Research, Development and Demonstration Plan:

- **Milestone 2:** Develop continuous in-line measurement for MEA fabrication. (4Q, 2012)
- **Milestone 3:** Demonstrate sensors in pilot scale applications for manufacturing MEAs. (4Q, 2013)
- **Milestone 4:** Establish models to predict the effect of manufacturing variations on MEA performance. (4Q, 2013)

Accomplishments

- Completed unplanned but promising experimentation on the use of ultrasonics for pressing of low-temperature (Nafion®) MEAs.
- Submitted two publications for review based on early unplanned experimentation and testing of low-temperature MEAs produced with both thermal pressing and ultrasonic pressing.
- Completed modifications of commercial ultrasonic press and construction of custom tooling for the needs of our experimentation.
- Completed a working model for manufacturing cost analysis of high-temperature MEA assembly.
- Completed testing of the first high-temperature PEM MEA produced with both ultrasonic welding and sealing.

Introduction

To realize the tremendous potential that fuel cell (FC) technology has to improve the world's environment and reduce our dependence on fossil fuels, it is essential that high-volume, high-quality manufacturing technologies are developed in parallel with the materials and designs for MEAs, stacks, and the other stack components, which is currently not the case. There are currently three main barriers to the development of high volume FC manufacturing.

The first major barrier is that the current practice involving extensive testing and burn-in of components and stacks will not allow the industry to achieve the necessary cost targets and throughput for stacks, components, and systems. It is not uncommon for stacks to undergo burn-in and qualification testing for as long as 24 hours or more. The costs of the test equipment, space, and personnel to execute these tests are a major barrier to the wide-spread adoption of FC technologies. FC researchers and industry must develop the materials, designs, and manufacturing processes necessary to totally eliminate the practice of 100% burn-in testing.

The second major barrier to high-volume FC production is the current processes used to press MEAs. For low-temperature (e.g. Nafion[®]) MEAs used in both PEMFCs and direct methanol (DM)FCs, it is common to thermally press for as long as 1½-5 minutes. While this process cycle time may be acceptable for prototype level testing and manufacturing, it is totally incompatible with economical high-volume manufacturing. Even the pressing process for high-temperature (polybenzimidazole, or PBI) MEAs, while much shorter than for Nafion[®]-based MEAs at less than one minute, is still too long for high-volume manufacture. It is also common for assembly of a single PEMFC stack to take as long as an entire day. MEA manufacturing unit process cycle times must be measured in milliseconds, or at most a few seconds, and stack assembly unit process cycle times must be measured in seconds or minutes, not hours.

The third major barrier impeding economical, high-volume FC production is the variability of MEA performance. The component materials, including gas diffusion layers (GDL) or gas diffusion electrodes (GDE), membranes or catalyst-coated membranes, and gasketing materials all exhibit variations in key properties such as thickness, porosity, catalyst loading, and water or acid content and concentration. Yet, it is common practice to employ a fixed combination of pressing process parameter values (time, temperature and pressure), regardless of these variations. As a result, MEAs exhibit variations in physical and performance related properties. Even though these MEAs may all perform acceptably in a single cell test fixture, when combined in a stack the variations in MEA properties may result in individual cells failing the performance test. As a consequence, stacks must frequently be disassembled and reassembled with replacement components or component locations re-ordered.

Although there are numerous manufacturing issues with other PEMFC and DMFC components that comprise a stack including (but not limited to) catalyst coating of GDL or membrane and bipolar plate manufacturing, one of, if not the main bottleneck to cost-effective, high-volume FC production is arguably MEA pressing.

Approach

The current state of practice in MEA manufacturing calls for the application of fixed pressing process parameters (time, temperature, and pressure), even though there are significant variations in in-coming material properties of the membrane and electrodes including thickness, mechanical properties, and acid/water content. MEA manufacturers need to better understand the relationships among those incoming material properties, the manufacturing process parameters, the resulting MEA physical and electrochemical properties, and the eventual electrical performance of the MEA in a stack.

We plan to address the problems associated with different methods of pressing high temperature MEAs, particularly PBI with phosphoric acid as the electrolyte, by applying APC techniques and ultrasonics. Through extensive experimentation and testing, we plan to develop analytical and empirical models of the relationships among incoming component material properties, the manufacturing process parameters, the resulting MEA properties, and the performance of the MEA in a stack.

With the knowledge gained and new hardware designs, we will then attempt to identify one or more key properties (such as electrochemical impedance spectroscopy response, porosity, spring constant, or direct current resistance) of the MEA that can be measured in situ during the thermal or ultrasonic pressing process, and then correlate these properties to the eventual physical and electrochemical performance of the MEA in a stack. If we are successful in identifying such an in situ measurement(s), adaptive control algorithms along with integrated process parameter and MEA performance sensing capabilities will be developed to allow us to vary the thermal and ultrasonic pressing process parameters in real time in order to achieve optimal uniformity of MEA performance.

We anticipate that the APC and processing techniques being investigated can be applied equally well, with certain modifications, to the pressing of both high-temperature and low-temperature MEAs, although the focus of this research and development work will be on the former because of our extensive experience with these materials and the enhanced performance they offer (e.g., high operating temperature, no water management issues, high CO and H₂S tolerance). Our research is not application specific as the results may be applied to a broad range of FC applications.

Results

We are in the first year of this multi-year research project. Our initial activities were focused on establishing and documenting experimental procedures

and MEA testing protocols, and the validation of those protocols by means of comparison of test results with baseline MEAs produced by our BASF partner. This has been successfully completed.

In order to gain experience with all of the experimental equipment we conducted an unplanned series of tests of low-temperature (Nafion® 117 membrane and BASF Fuel Cell 250EWALT electrodes with 0.25 mg/cm² catalyst loading) MEAs produced with both thermal and ultrasonic pressing. Thermal press parameters were taken from various suggested values in the literature. The process parameters of time, temperature and pressure for thermally pressed MEAs and energy, pressure, amplitude, and time for ultrasonically pressed MEAs were not optimized. The resulting MEAs were tested under the following conditions:

- Startup consisted of 1 hr burn-in at 23°C and 0.2 A/cm² with cathode and anode humidification at 35°C.
- H₂ and air flow rates were both 100 ml/min.
- Polarization curve taken at 30°C operating temperature.
- Operating temperature was then raised to 80°C with anode and cathode humidifiers at 85°C.
- Second polarization curve taken after running at 0.2 A/cm² for several minutes.

For the thermal pressed MEAs the following observations were made:

- Increased sealing time resulted in a slight improvement in MEA performance at 30°C but essentially no improvement at 80°C.
- The middle sealing temperature (140°C) yielded optimum MEA performance at both 30°C and 80°C.
- The middle sealing pressure (50 kg/cm²) yielded the optimum MEA performance at both 30°C and 80°C.

For the ultrasonically pressed MEAs we observed that high sealing pressure yielded the best MEA performance at 30°C, while there was little difference in MEA performance at 80°C.

As a comparison, for our very limited tests the thermal pressed MEA performed better at 80°C, while the ultrasonically sealed MEA performed better at 30°C.

The major portion of our research during Fiscal Year 2009 has focused on investigating the feasibility of the novel ultrasonic bonding of MEA materials to significantly reduce unit process cycle times, achieve a major reduction in energy consumption, and reduce the cost of manufacturing high-temperature PEM MEAs. Among the many major challenges that are being addressed are:

- What are the best ultrasonic horn materials and design?
- What are the optimal anvil materials and design?
- What are the limits on allowable power/energy to prevent material damage?
- What are the best methods for process controls (e.g. energy mode, collapse mode, absolute mode)?
- How to meet dimensional tolerance requirements?
- Is it possible to meet the target cycle time of <1 sec?
- Are there any feasible rapid (ms level) sensing modes for use in the application of adaptive process controls for ultrasonic pressing?

Currently the bonding (welding) of electrodes to sub-gaskets for high-temperature PEM MEAs is performed in a heated press with a cycle time of about 1 minute. As a result of our investigation we have demonstrated that a unit process cycle time of less than one second is possible, and the resulting weld has a pull strength equal to or greater than that of a thermal weld. Of particular note, the energy consumed by ultrasonic welding is less than 5% of the energy consumed by thermal welding. We plan to conduct a full factorial design of experiments to optimize the weld process parameters.

The more challenging process for ultrasonics is the sealing of the electrodes to the PBI membrane. Figure 1 shows the experimental tooling (horn and anvil) being used in our investigations. Figure 2 shows a destructive test of an ultrasonic seal. The very good bond between the GDE and PBI membrane can be clearly seen in this photo. Figure 3 shows a 50 cm² MEA design used in all of our design of experiments for both thermal and ultrasonic sealed MEAs. We have produced and tested our first high-temperature PEM MEA using ultrasonics for both welding and sealing. Figure 4 shows

FIGURE 1. Experimental Seal Tooling for Ultrasonic Sealing of MEAs

FIGURE 2. Destructive Test of GDE-PBI Membrane Ultrasonic Seal

FIGURE 3. Standard 50 cm² MEA used for Design of Experiments

the polarization curve for this MEA, tested with both H₂-O₂ and H₂-Air, operated at 160°C. Also shown is the baseline specification performance from BASF Fuel Cell for their thermal pressed MEA operating with H₂-air at 160°C. As can be seen the ultrasonic sealed MEA operating with hydrogen and oxygen performs well, while the MEA operating with hydrogen and air shows greater losses in both the ohmic loss and the mass transport loss regions of the curve. This is likely caused by damage done to the catalyst layer by the ultrasonic sealing process. It should be noted, however, that we have not yet completed our design of experiments and have not tried to optimize the ultrasonic sealing process parameters. Of equal interest, however, is the fact that the activation losses for the ultrasonic sealed MEA are significantly less than for the baseline MEA. If this holds true for other ultrasonic sealed MEAs this could be a major advantage of the use of ultrasonic sealing.

FIGURE 4. Performance Curve for Ultrasonically Welded and Sealed MEA

Conclusions and Future Directions

Although the results are very preliminary and we have not completed our design of experiments we are very encouraged by the performance we have achieved with our first ultrasonic-sealed high-temperature PEM MEA. We are optimistic that we will succeed in achieving a major reduction in unit process cycle time for MEA pressing, and a corresponding major reduction in energy consumed by this critical MEA manufacturing process. We may also realize an unexpected improvement in activation loss, if our initial test is an indication of an inherent benefit for ultrasonic sealing.

Major activities planned for the remainder of Phase I include:

- Completion of our design of experiments for both thermal and ultrasonic-sealed MEAs.
- Modeling of the relationships among incoming MEA properties, manufacturing process parameters, and MEA performance.
- Investigation of various in situ sensing modes that might be used for feedback control during the sealing process.
- Design and experimentation of adaptive process control techniques.
- Cell level testing of MEAs produced using optimized process parameters.
- Completion of manufacturing cost analysis and establishment of cost targets for Phase II.

FY 2009 Publications/Presentations

- Walczyk, D., Share, D., Krishnan, L., Snelson, T., Puffer, R., "The Performance of Thermally and Ultrasonically Sealed Membrane Electrode Assemblies of Low Temperature PEM Fuel Cells," Accepted for publication in *Proceedings of the*

ASME International Manufacturing Science and Engineering Conference (MSEC) 2009.

- Walczyk, D., Share, D., Krishnan, L., Snelson, T., Puffer, R., “The Performance of Thermally and Ultrasonically Sealed Membrane Electrode Assemblies of Low Temperature PEM Fuel Cells,” Submitted for review in the *ASME Journal of Fuel Cell Science and Technology*.

VI.7 Development of Advanced Manufacturing Technologies for Low Cost Hydrogen Storage Vessels

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Contract Number: DE-FG36-08GO18055

Subcontractor:

Boeing Research and Technology, Seattle, WA

Partners:

- Lawrence Livermore National Laboratory (LLNL), Livermore, CA
- Pacific Northwest National Laboratory (PNNL), Richmond, WA

Project Period: September 26, 2008

Project End Date: October 31, 2011

Contribution to Achievement of DOE Manufacturing Milestones

This project is directed to develop a hybrid manufacturing process, which combines filament winding and automated fiber placement processes to save composite material usage in Type IV hydrogen storage vessels. Further efforts focus on a dry-tape technology having the potential to significantly reduce vessel production cycle time. It will contribute to achievement of the following DOE milestones from the (3.5) Manufacturing R&D section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- **Milestone 24:** Develop fabrication and assembly processes for high-pressure hydrogen storage technologies that can achieve a cost of \$2/kWh. (4Q, 2015)

Accomplishments

- Investigated and selected candidate materials for use in both filament winding and automated fiber placement;
- Investigated an optimized liner dome profile; manufactured liners and measured their profiles;
- Designed and built robotic automated fiber placement system;
- Generated the first iteration of composite material design in the vessel structure; and
- Developed a cost model to assess cost sensitivities for different manufacturing techniques.

Project Objective

Develop new methods for manufacturing Type IV pressure vessels for hydrogen storage with the objective of lowering the overall product cost, which will:

- Optimize composite usage by combining traditional filament winding and automated fiber placement techniques.
- As a parallel effort, investigate emerging dry-tape technology which could drastically shorten the manufacturing time.

Technical Barriers

The project addresses the following technical barriers from the Hydrogen Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) System Weight and Volume
- (B) System Cost

Introduction

The goal of this project is to develop an innovative manufacturing process for Type IV high-pressure hydrogen storage tanks, with the intent to significantly drive down costs. Part of the development is to integrate the features of high precision automated fiber placement (AFP) and commercial filament winding (FW). As a potential, high-risk approach, 'dry-tape' technology is being investigated by LLNL, which could shorten production cycle time.

To achieve the goal of integrating AFP and FW, Quantum and Boeing have:

- (a) Evaluated towpreg materials to address the material compatibility issue.

- (b) Investigated liner dome profile optimization.
- (c) Manufactured liners and measured liner profile for vessel production purpose.
- (d) Assembled and integrated the AFP system, and further developed the control software.

Quantum and Boeing plan to build and burst test the first vessel by the end of this calendar year. Furthermore, we will continue to work on composite design iterations and refinement of the AFP process. Quantum and Boeing will supply manufacturing cost information to PNNL to refine the Cost Model, which will assess the cost sensitivities of this manufacturing technique. In a parallel activity, LLNL may conduct experiments to prove the feasibility of dry-tape technology. PNNL and LLNL will report their activities in separate reports.

Approach

Type IV pressure vessels are commonly made by FW with a limitation that the reinforcement has to be altogether continuous: the placement of material on the dome regions inevitably introduces materials on the entire cylinder region. Materials introduced this way are not needed and are called “parasitic”. This parasitic material lowers the system storage efficiency and increases cost. The proposed process can locally reinforce the dome regions, eliminating parasitic waste. This is done by incorporating the AFP process, which can place non-continuous material on any region of the tank to supplement the FW process. Thus, this project integrates the efficiency benefit of AFP with the speed of FW to create a new hybrid process which can optimize composite usage. Because these two processes typically use different materials, studies have been performed to address compatibility. Both materials have to cure completely within the existing processing window and the overlap between them must transfer load efficiently. A detailed composite design will determine the quantity and distribution of the materials in the vessel introduced by each process. The AFP process will be adapted to pressure vessel production to take advantage of its efficient material usage.

Results

Since the project started, Quantum and Boeing have built coupons and evaluated shear strength and fracture toughness. The test results have guided our composite design, by indicating how much overlap is needed between the AFP and FW placed materials. We have also studied the cure behavior for both materials to verify a complete cure.

We have developed an optimized liner dome profile for uniform fiber stress distribution, and have manufactured high-density polyethylene liners according

to this derived profile. The liner surface profile was measured using a coordinate measuring machine to verify the accuracy of the liner production process. This same dome profile will be used in the path generation for AFP process, in order to place the material in the desired location. Quantum is working on the composite design using stress analysis and finite element modeling. We have generated the first iteration design, according to which the non-continuous materials will be laid down in the AFP process first on the dome region locally (shown in Figure 1), and then FW is used to cover continuous composite material all over the vessel surface. Based on our current composite design results, approximately 6 kg of materials may be eliminated from the current 76.5 kg design.

A graphic illustration of Boeing's robotic arm and revised head for AFP is shown in Figure 2.

The DOE target for system storage efficiency is based on the assumption of producing 500,000 units per year. A system considered here consists of a single 129L type IV H₂ tank (approximately 5 kg hydrogen capacity) with a solenoid valve, a set of high pressure and low pressure regulators, a mid stage valve, a receptacle with filter, all tubing and fittings for this system, a frame, a wire harness, a pressure sensor and a balance of parts (consisting mainly of fasteners etc.). The end-user cost efficiency of such a system based on the assumption of 500,000 units/year as well as the assumption that 1 kg hydrogen is able to generate 33.3 kWh energy, is estimated to be \$45.9/kWh, with a weight efficiency of 1.50 kWh/kg. The 6 kg of composite savings will improve the storage system weight efficiency

FIGURE 1. Local Dome Reinforcement

FIGURE 2. Kuka KR100 Robot Platform with AFP Integration

approximately to 1.58 kWh/kg, and will possibly improve the system cost efficiency as well.

The overall AFP robotic system is 90% complete for this project. Key to this system is a Boeing designed tow-placement head having a low-profile that allows for a tight clearance to the end bosses. The head uses six-tows, each 0.25-inch wide producing a 1.5-inch band. The machine can add an individual tow independently from each other. The integrated system includes a 6-spool creel mounted on the upper arm of the robot. The robot's path is driven by CGTech-VCP software adapted for a hybrid fiber-placement/filament-winding process. The post-processor for the path generation software has been completed. Boeing has further completed the liner mounting system, which will be used for future development activities. Final tasks prior to first tank build include:

- (1) Reworking a limited number of creel components.
- (2) Completing the Kuka controller's input/output mapping .
- (3) Testing programs and end-dome material lay-down. Once the system has been demonstrated, Boeing will begin increasing rates to evaluate productivity goals.

We will build the first hybrid process vessel and perform the burst test according to European Integrated Hydrogen Project standard before the end of the current calendar year. After the test, we will continue composite design iterations and improvements in the AFP process capabilities.

We also supply manufacturing cost information to help PNNL assess cost sensitivities of different manufacturing techniques.

Conclusions and Future Direction

- Material study, initial composite design, and liner dome investigation have been finished.
- The AFP equipment and software is 90% complete; completion of this task will allow the manufacture of the first hybrid AFP/FW pressure vessel.
- Further composite design iterations and AFP process development will be required to refine the process (Phase II activities).
- Identified and prioritized the significant manufacturing costs with consideration of process steps, materials, equipment, factory space and labor for compressed hydrogen storage tank (details reported separately on "Design of Advanced Manufacturing Technologies for Low Cost Hydrogen Storage Vessels" by PNNL).

FY 2009 Publications/Presentations

1. Development of Advanced Manufacturing Technologies for Low Cost Hydrogen Storage Vessels, Annual Merit Review, Department of Energy, May 18–22, 2009, Arlington, VA.

VI.8 Inexpensive Pressure Vessel Production Through Fast Dry Winding Manufacture

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Start Date: August 30, 2008
Projected End Date: August 30, 2011

Objectives

- Demonstrate novel pressure vessel production process.
- Project cost advantages of new process.

Technical Barriers

This project addresses the following technical barrier from the Manufacturing R&D section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

(H) Lack of Carbon Fiber Fabrication Techniques

TABLE 1. Progress toward Meeting DOE On-Board Hydrogen Storage Technical Targets

Lawrence Livermore Tape-Fabricated Vessels					
Storage Parameter	Units	2010 Target	2015 Target	2009 Proof of Concept ¹	2011 Projected Best Cost ²
Storage System Cost	\$/kWh	4	2	~10	~5

¹ Using graphite prototype tape, estimate based on mass production rates (if proven)

² Estimate based on most favored fiber and mass production capital

Accomplishments

- Designed experiment capable of proving mass production rate.
- Coordinated planning with other members of the Tank Manufacturing team.

- Protected intellectual property through patent application.

Introduction

As a universal transportation fuel that can be generated from water and any energy source, hydrogen (H₂) is a leading candidate to supplant petroleum with the potential to ultimately eliminate petroleum dependence, associated air pollutants and greenhouse gases. The predominant technical barrier limiting widespread use of hydrogen automobiles is storing enough hydrogen fuel onboard to achieve sufficient (500+ kilometers) driving range in a compact, lightweight, rapidly refuelable, and cost-effective system. Pressure vessels provide a necessary contribution to solving this challenge in the near term, but also contribute most of the cost and weight of a hydrogen storage subsystem. In collaboration with industrial partners on a DOE funded manufacturing technologies team, we are addressing the remaining cost efficiency hurdles to enable a rapid transition to hydrogen-fueled automobiles. Our contribution is a novel manufacturing process that may offer substantial manufacturing cost savings independent of the choice of fiber material.

Approach

The novel composite manufacturing process being researched and developed at LLNL has the potential for considerable savings in pressure vessel cost. Although this process has details that remain proprietary, it has numerous resemblances to proven composites manufacturing processes. Figure 1 outlines the composite manufacturing process choices, with LLNL's novel tape technology on its rightmost edge. Other efficient approaches to vessel manufacture (wet wound, fiber placement) are being researched by team members (Quantum Technologies and Boeing). Alternatives at the left of the figure lead to undesirable characteristics.

LLNL's novel process combines many of the features of proven high-strength processes, except that it seeks to perform them at high speed to drastically reduce manufacturing cost. Other features and drawbacks of the tape process could affect materials costs and vessel performance, but the effects are likely to be slight and positive. Until the reality of significant manufacturing cost improvements is proven, the investigation of vessel performance effects and potential restrictions on fiber choices would be inconsequential. Therefore LLNL is

FIGURE 1. Bubble diagram dissects the various options for manufacturing composite vessels, starting from choices of the geometry of the individual composite fibers. Two undesirable characteristics of the final composite part are shown at the left of this diagram. The team of pressure vessel innovation partners (Quantum Technologies, Boeing, and Pacific Northwest National Laboratory) seeks to combine characteristics of wet winding and fiber placement, both of which avoid the undesirable consequences. LLNL's proposed novel tape technology, also on the right of this diagram, avoids the negative consequences and combines features of two proven processes being improved by team members.

proceeding to rapidly determine how much our novel process might save in just the manufacturing (capital and labor) cost. Figures 2 and 3 break that cost down in a fundamental way, first into what the process equipment adds to manufacturing cost as a function of how much material goes through a costly piece of production equipment how fast (the 'throughput'), and then how much 'throughput' that equipment can achieve when laying down a tape of a particular cross section at a particular speed. Attempts are made in these figures to roughly characterize our process with the conventional competing process – wet winding – while protecting proprietary process specifications.

Results

Our results to date from six months of funded research include various collaborations and plans for future collaborations with other team members. These provide a potential adoption path from LLNL to the most expert and incentivized pressure vessel manufacturers. Other results that are harder to report include intellectual property protection, which will only be complete when the patent office acts on LLNL's patent application. The central activity that has occupied LLNL researchers is the preparation of safety

FIGURE 2. Cost to perform a composite manufacturing process versus the composite material processing rate ('throughput' in units of mass-per-unit-time), at various levels of production capital cost (presuming a three year return on investment). This graph applies to all composite manufacturing processes, with conventional wet winding processes occurring in roughly the middle of its left hand edge. LLNL's novel dry tape process projects operation in the middle of the bottom edge of this graph, but actual specifications are deliberately not exact (by > 1 order of magnitude) to protect proprietary process technology.

FIGURE 3. Tape material processing rate ('throughput' in units of mass-per-unit-time) as a function of tape velocity, at various levels of tape cross sectional area. This graph applies to all continuous filament fiber production processes, and current wet winding processes occupy the lower left corner. LLNL's novel dry tape process projects operation in the upper right corner of this range, but actual specifications are deliberately not exact (by >1 order of magnitude) to protect proprietary process technology.

and cleanliness arrangement sufficient for the proof of concept experiment we intend to perform over the next few months.

Although many fiber and matrix material choices should be compatible with LLNL's tape innovation, very few provide the confidence to quickly perform our proof of concept experiments. In particular, the repeatability of (rapidly testable) bonding is at risk from airborne contamination and perhaps from humidity. Low material sensitivity to environmental conditions is therefore important. Facilities have been approved to meet these challenges, and plans to procure proprietary tape and (slightly hazardous) bonding materials have been approved that are compatible with our laboratory.

Our proof of concept experiment is focused on determining bonding speed – the key parameter limiting winding velocity. Figure 4 shows a block diagram schematic of the calorimeter designed for a proof of concept test apparatus. This design is not arbitrary; it is the simplest way to make measurements of a high-speed process without the measuring instrument limiting how fast the process can occur. Its approach relies

FIGURE 4. Schematic diagram of calorimeter to determine tape bonding speed by capturing temperature rise due to bonding with a digital oscilloscope. This hardware diagram mixes physical components, optical beam paths including captured photons in fibers, and electronics.

on the heat being evolved by a tape bonding process to find out how fast that process is occurring, without interfering with the mechanical phenomena that ought to be changing as a bond is forming (as might be the case with speed of sound, ultrasonic impedance, or opacity measurements), or further restricting the choice of experimental gas environment. Figure 5 shows the key components of the high-speed calorimeter now under construction, which are thermal isolation trusses that retain their dynamic calibration as stuck-together tape test specimens are bonded and taken out of the instrument.

FIGURE 5. Thermal isolation truss components of apparatus under construction. These truss stages mount tape specimens (black squares in the center of clear microscope cover slides, glued atop these trusses). One of these trusses is inverted and its tape specimen placed in abrupt contact with the other tape specimen to determine bonding speed with the calorimeter apparatus of Figure 4.

Conclusions and Future Directions

- We are conducting experiments to prove the processing rates of a novel composite manufacturing process. If these experiments are successful at showing rates capable of high-speed mass production, they will be extended to prove lack of detrimental effects when applied to pressure vessel manufacture.
- In collaboration with industrial partners on a manufacturing technology team, we are addressing the cost advantages of major improvements in pressure vessel manufacturing processes.

FY 2009 Publications/Presentations

1. Poster Presentation, Hydrogen, Fuel Cells and Infrastructure Technologies Program Annual Merit Review, Arlington, VA, May 20, 2009.

VII. SYSTEMS ANALYSIS

VII.0 Systems Analysis Sub-Program Overview

Introduction

Systems Analysis supports decision-making by providing a greater understanding of technology gaps, options and risks, and the contribution of individual technology components to the overall system i.e., from fuel production to utilization, as well as the interaction of the components and their effects on the system. Analysis is also conducted to assess cross-cutting issues, such as integration with the electrical sector and use of renewable fuels. Particular emphasis is given to assessing fuel quality impacts on fuel cell performance and infrastructure implications.

The Systems Analysis activity made several significant contributions to the Hydrogen, Fuel Cells and Infrastructure Technologies (HFCIT) Program during Fiscal Year 2009. Several analytical tools including the Stationary Fuel Cell Power Model, Agent-Based Model and Macro-System Model (MSM) were completed and peer reviewed to support the analytical process. Resource, infrastructure and early market analyses were conducted to better understand supply and demand issues. Analysis of environmental impacts of hydrogen on the atmosphere was completed in FY 2009 which showed minimal impacts on atmospheric conditions. Hydrogen quality was modeled and evaluated to examine the impact on fuel production cost to achieve the quality specifications required for the fuel cell to maintain performance and durability. The Greenhouse gases, Regulated Emissions and Energy use in Transportation (GREET) model was modified to enable greenhouse gas emissions and petroleum use to be evaluated on a well-to-wheels (WTW) basis for fuel cell vehicles in comparison to other options such as plug-in hybrid vehicles.

Goal

Provide system-level analysis products to support the overall Program by evaluating technologies and pathways, guiding the selection of research, development and demonstration projects, and determining technology gaps, risks and benefits.

Objectives

- By 2011, enhance the MSM to include the stationary electrical generation and infrastructure.
- By 2014, complete environmental studies that are necessary for technology readiness goals.
- By 2015, analyze the potential of fuel cells for multiple applications such as portable, stationary, and backup power generation. The analysis will address necessary resources, infrastructure, and interactions with electrical sectors.
- Provide analysis of Program milestones, including risk analysis, independent reviews, financial evaluations and environmental analysis, to support the Program's needs prior to the technology readiness milestone.
- On an annual basis, update the WTW analysis for technologies and pathways for the overall Program by including technological advances or changes.

FY 2009 Status

Systems Analysis was established within the Program to develop a consistent, comprehensive framework for examining the economics, benefits, risks, opportunities, and impacts of fuel cells and renewable fuels. Analysis was also conducted in FY 2009 to identify early markets for fuel cells and opportunities to reduce cost through various mechanisms, such as tax credits and other legislation.

FY 2009 Accomplishments

- The MSM, a dynamic engineering transition model, was updated to include new hydrogen production pathways. The model is used for the simulation of the performance and evolution of hydrogen infrastructure using a distributed architecture to link existing and emerging models for system components. The model was used to analyze the delivered hydrogen cost, WTW parameters (greenhouse gas emissions, petroleum energy use and total energy use) and hydrogen losses for several pathways. The new models added to the MSM were the resources model, HyDRA, the infrastructure model, HyPRO, and the updated delivery model, HDSAM.
- Oak Ridge National Laboratory performed sensitivity analysis with the HyTrans model based on the previously published scenario analysis to understand the sensitivity of the fuel cell vehicle penetration to the vehicle on-board storage targets. This analysis showed the vehicle penetration rates would be reduced from 95% to 50% by 2050 if storage research and development was only capable of attaining a storage cost of \$17/kWh versus the target of \$2/kWh.
- The H2A Stationary Power Model was developed and reviewed by industry, academia and national laboratories to address combined heat and power generation for proton exchange membrane, phosphoric acid and molten carbonate fuel cells. The model features analysis of power, heat and hydrogen fuel costs based on capital equipment costs, feedstock prices, operating climate conditions and the heat and power loads for demand systems. The format of the model features a graphical user interface for data input. The model and fuel cell analysis cases will be posted on the Energy Efficiency and Renewable Energy Web site for public access in the fourth quarter of FY 2009.
- The WTW analysis capabilities were enhanced by modifying the GREET model to include conventional and alternative fuel plug-in hybrid electric vehicles. The plug-in vehicle represents the emerging technology for comparison to the vehicle technology portfolio. The analytical capabilities also include the comparison of plug-in hybrid electric vehicles with fuel cells. The WTW analysis enables the evaluation of greenhouse gas emissions for various electrical sources such as U.S. average, California, and Illinois grid mixes. An example is shown below with the U.S. grid mix which shows that plug-ins with fuel cells would have lower greenhouse gas emissions than conventional fuel plug-in vehicles.

Source: Argonne National Laboratory

Note: The source of electricity for the "PHEV FC Electrolysis" pathway is U.S. grid mix electricity.

ICEV – internal combustion electric vehicle; PHEV – plug-in hybrid electric vehicle; SI – spark ignition; FC – fuel cell, CI – compression ignition; SMR – steam methane reformer; E85 – 85% ethanol, 15% gasoline; GHG - greenhouse gas

- Argonne National Laboratory developed a model for analyzing the impact of hydrogen quality on fuel cell performance and the hydrogen production costs associated with meeting the required hydrogen quality specifications. The hydrogen production technologies modeled included distributed natural gas and auto-thermal reforming. Analysis showed that key impurities such as carbon monoxide and sulfur required to sustain fuel cell performance can be removed with adjustment to operating parameters of separation equipment associated with the production technologies. The impact of meeting the hydrogen quality specifications resulted in a cost increase of less than \$0.05/gasoline gallon equivalent.
- Water Analysis: The analysis of the impact of water on a future hydrogen economy, including the economic impact of water prices on hydrogen production and the impact of hydrogen production on regional water resources has found water to have minor impacts on hydrogen deployment. The assessment included an initial examination of water permitting on water cost but was found to be region-specific and highly contentious so in-depth analysis was not pursued. Instead a methodology was developed for determining the upper bound for hydrogen cost with respect to water use.
- Pacific Northwest National Laboratory analyzed the commercial benefits of the HFCIT Program by tracking the commercial products and technologies developed from the support of the Program. The results show that over 140 patents were awarded and over 20 products were commercialized as a result of research funded by HFCIT in the areas of storage, production, delivery and fuel cells.

Budget

The budget for the Systems Analysis activity is consistent with the goals and objectives of the sub-program and is responsive to assessing early market opportunities for fuel cell applications. The FY 2010 budget request includes funding for resource and infrastructure analysis, as well as fuel quality evaluation, environmental analysis, overall program analysis, modeling, and systems integration.

FY 2010 Plans

The Systems Analysis activity for FY 2010 will focus on conducting analyses to determine technology gaps for fuel cell systems and infrastructure for different applications. Analyses will be focused on understanding the tradeoffs and regional impacts of fuel cells with other alternative fuels and the electrical sector on a WTW basis, and the synergies of linking stationary fuel cell power generation with the electrical sector. The FY 2009 appropriation included \$7.7 million for Systems Analysis; the FY 2010 request is \$5 million. The budget request for FY 2010 reflects the focus on early market analysis, fuel cell technology evaluations, renewable fuel benefits, as well as resource and infrastructure analysis.

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VII.1 HyDRA: Hydrogen Demand and Resource Analysis Tool

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Subcontractor:
A Mountaintop LLC, Lakewood, CO

Project Start Date: October 1, 2006
Project End Date: September 30, 2011

Objectives

- Develop a Web-based geographic information system (GIS) tool to allow analysts, decision makers, and general users to view, download, and analyze hydrogen demand, resource, and infrastructure data spatially and dynamically.
- Provide a repository for hydrogen spatial data inputs and model results.
- Display and aggregate the results of spatial analyses.

Technical Barriers

This project addresses the following technical barriers from the Systems Analysis section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (B) Stove-Piped/Siloed Analytical Capability
- (C) Inconsistent Data, Assumptions, and Guidelines
- (D) Suite of Models and Tools

Contribution to Achievement of DOE Systems Analysis/Systems Integration Milestones

This project will contribute to achievement of the following DOE milestones from the System Analysis and Systems Integration sections of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- **Milestone 5 (System Analysis):** Complete analysis and studies of resource/feedstock, production/

delivery and existing infrastructure for various hydrogen scenarios. (4Q, 2009)

- **Milestone 8 (System Analysis):** Complete analysis and studies of resource/feedstock, production/delivery and existing infrastructure for technology readiness. (4Q, 2014)
- **Milestone 27 (System Analysis):** Complete the 2nd version of the Macro-System Model to include the analytical capabilities to evaluate the electrical infrastructure. (2Q, 2011)
- **Milestone 15 (Systems Integration):** MSM analysis test cases. (4Q, 2006; 3Q, 2009; 4Q, 2010)

Accomplishments

- Completed initial integration with Macro System Model (MSM) to produce six new spatial data layers of cost, energy, and greenhouse gas (GHG) emissions for forecourt electrolysis. Provided a proof-of-concept for MSM integration with spatial models.
- Completed development and deployment of new HyDRA Web 2.0 architecture, which provides improved user experience and a single data store for all layers. The new architecture will also allow for dynamically sending and receiving data to and from other hydrogen models, such as MSM.
- Implemented 69 spatial data layers related to hydrogen resource, infrastructure, and demand. Datasets represent spatial data input layers, and output from spatial analyses.
- Registered 118 users who have accessed the HyDRA application in Fiscal Year 2009.

Introduction

The HyDRA tool was developed to conduct dynamic geographic analysis of hydrogen processes in Web-based environment. This capability is important as resource, demand, and infrastructure will vary regionally for hydrogen production, delivery, and dispensing. HyDRA provides a repository for storing spatial data used by hydrogen analyses and tools, and allows spatial analysis results to be compared from a common application.

Approach

The HyDRA tool is a state-of-the-art, Web 2.0 application that has the look, feel, and functionality of a traditional client-based GIS application. It provides

the capability to view hydrogen data and how they vary across the United States on a regional basis. HyDRA provides analysis results in the form of a map, instead of a number. It is available at <http://rpm.nrel.gov>. Users can view spatial hydrogen data and interact with the maps to create custom analyses. Data can be downloaded from the application and used in other analyses. To ensure HyDRA's usability, NREL recently redesigned it from its original code base to provide an easier to use, more intuitive interface. Users will be able to create their own spatial datasets and upload them into the HyDRA tool to create a completely customizable and dynamic analysis tool.

Spatial data layers are at the core of the HyDRA application. Currently, 69 datasets have been created. The data layer categories include resource cost and availability, hydrogen production potential, hydrogen production cost, resource consumption, hydrogen demand, infrastructure, and results from integration with other hydrogen models.

Results

The major HyDRA efforts that have been completed this year are the integration of HyDRA with the MSM and the completion of building the model on a new architecture.

The integration with MSM created six new layers displaying the cost, energy usage, and GHG emissions of forecourt electrolysis. This initial proof-of-concept integration was achieved by manually exchanging data between the models. The input to the MSM was a county level industrial electricity cost layer and a state level based grid mix layer from the Environmental Protection Agency (EPA) eGRID [1]. After processing the provided data in the MSM, six new spatial data layers were provided back to HyDRA: cost (on a state and county basis), well-to-wheel energy use, petroleum use, fossil energy use, and well-to-wheel GHG

emissions. These new data layers allow users to determine where low-cost, low-energy use, low-emission hydrogen can be produced via forecourt electrolysis. Figure 1 illustrates the integration process.

In anticipation of HyDRA dynamically integrating with the MSM and other models in the future, the application was moved to the new OpenCarto architecture. In addition to providing programmatic integration capability, this architecture provides for a better user experience by providing a more intuitive interface, quick response times, and the ability to use Google maps to view data from street level to the entire world. Figure 2 shows the old version of HyDRA versus the new version of HyDRA.

The HyDRA architecture allows users to interact with maps dynamically to perform custom analyses. Users can zoom, pan, measure, find a location, adjust transparency, and print. Multiple layers can be turned on simultaneously, and then be thresholded so that only certain values presented on the map can be seen. Data can be queried on the map, viewed in a spreadsheet format, and downloaded for additional analysis. Metadata for layers can be viewed and referenced from the layer tree. Figure 3 shows an example of how HyDRA can be used to perform spatial analyses. The screenshot shows the demographic demand and the potential methane available from manure management in the northeastern United States. The application limited the demand classes displayed to just show Good, Very Good, High, and Very High demand. It has also been limited to show methane available from manure management greater than 2,000 tonnes/year/county. The screenshot shows that demand and resource are geographically proximate in southeast Pennsylvania, near Chicago, and in Ohio.

A second example analysis makes use of the new MSM data layers by examining where forecourt hydrogen could be produced inexpensively with low emissions in an area with high potential early demand.

FIGURE 1. Process for the Manual Integration of HyDRA and the MSM

FIGURE 2. HyDRA's Initial Architecture (top) Contrasted with The New Architecture (bottom)

FIGURE 3. Analysis of Demand and Biomethane Potential in the Northeastern United States

Figure 4 shows HyDRA displaying industrial electricity prices less than \$50/MWh, early high to very good demand for hydrogen as a transportation fuel, and total GHG energy usage for forecourt electrolysis, by state, less than 8,000 Btu/mile. As highlighted, the Pacific northwest looks to be an area of the United States with good potential for clean forecourt electrolysis.

Data provides the core of HyDRA's capability and the datasets currently available represent spatial source data and hydrogen analysis results. Available data is categorized in the following and the number of datasets in each category is represented in parentheses.

FIGURE 4. Analysis of Low-Cost, Low-Emission, High-Demand Forecourt Electrolysis

Source Data

- Roads, cities, states, counties (6)
- National Energy Modeling System, HyDS regions (2)
- Electric and natural gas rates (6)
- Solar, wind, biomass, geothermal, hydropower resources (5)
- Nuclear, coal (3)
- Biomass potential (5)
- Infrastructure (12)
- Imagery (1)

Hydrogen Analysis Results

- Hydrogen demand (3)
- Forecourt steam methane reformer and electrolysis cost (6)
- Biomass, solar, geothermal, hydropower and wind hydrogen potential (8)
- Nuclear, coal, natural gas hydrogen potential (6)
- MSM cost, energy and GHGs (6)

Conclusions and Future Directions

HyDRA provides a single point of reference for spatial data related to hydrogen. The improved user interface provides for a better look and feel and user experience. In the future, the ability to connect dynamically with other hydrogen models will allow hydrogen analysts to use consistent data inputs, and comparable analytical results. In the future HyDRA will:

- Develop the capability to generate dynamic layers in the HyDRA application from user and model provided data.

- Develop and deploy basic analysis functions such as graphing, changing underlying assumptions, and buffering.
- Integrate with other hydrogen models and analyses to develop new data input layers and display model results using manual and dynamic integration.
- Create case studies to ease user analysis, similar to H2A cases.

FY 2009 Publications/Presentations

1. Sparks, W., Levene, J., Helm, C. (2009) Hydrogen Demand and Resource Assessment. 20 pp.; NHA Conference and Hydrogen Expo.
2. Helm, C., Levene, J., Sparks, W., Hostetler, M. (2008) Facilitating Code Reuse for the Rapid Deployment of Web Mapping Applications at the National Renewable Energy Laboratory (NREL). 1 p.; Poster presentation at American Geophysical Union Fall Meeting.
3. Sparks, W. (2009) OpenAtlas – A Foundation for the Geospatial Web. 22 pp.; Podium presentation at National Laboratories Information Technology Summit.

References

1. eGRID, Clean Energy, US EPA: <http://www.epa.gov/cleanenergy/energy-resources/egrid/index.html>.

VII.2 Water Needs and Constraints for Hydrogen Pathways

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Project Start Date: October 1, 2007

Project End Date: October 1, 2009

Objectives

- Quantify the impact of water (cost, quality, scarcity) on a future hydrogen economy.
- Quantify the impact of a future hydrogen economy on national and regional water resources.
- Document best practices for hydrogen stakeholders in system design and feedstock management with respect to water.

Technical Barriers

This project addresses the following technical barriers from the Systems Analysis section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) Future Market Behavior
- (D) Feedstock Issues

Contribution to Achievement of DOE Systems Analysis Milestones

This project will contribute to achievement of the following DOE milestones from the Systems Analysis section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- **Milestone 1:** Complete evaluation of the factors (geographic, resource availability, existing infrastructure) that most impact hydrogen fuel and vehicles. (3Q, 2005)

- **Milestone 5:** Complete analysis and studies of resource/feedstock, production/delivery and existing infrastructure for various hydrogen scenarios. (4Q, 2009)
- **Milestone 11:** Complete environmental analysis of the technology environmental impacts for the hydrogen scenarios and technology readiness. (2Q 2015)
- **Milestone 27:** Complete the 2nd version of the Macro-System Model to include the analytical capabilities to evaluate the electrical infrastructure. (2Q, 2011)

Accomplishments

- Constructed a spreadsheet model that calculates water withdrawal and consumption for hydrogen process and cooling water from hydrogen process parameters and water supply quality data.
- Estimated cost of water management equipment for the four most likely hydrogen production pathways (forecourt and distributed, steam methane reformer [SMR] and electrolysis).
- Calculated economic tradeoff between water use and investment in water-saving technologies by integrating water technology analysis with H2A model.
- Working with the National Renewable Energy Laboratory (NREL) and Sandia National Laboratories (SNL) to incorporate water analysis into the Macro-System Model (MSM).
- Working with SNL to incorporate SNL's model of national and regional water resources with hydrogen rollout scenarios.

Introduction

Water is a critical feedstock in the production of hydrogen. In fact, water and many of the energy transformations upon which society depends are inextricably linked. Approximately 39% of freshwater withdrawals are used for cooling of power plants, and another 8% are used in industry and mining (including oil and gas extraction and refining). Major changes in the energy infrastructure (as envisioned in a transformation to a hydrogen economy) will necessarily result in changes to the water infrastructure. Depending on the manner in which a hydrogen economy evolves, these changes could be large or small, detrimental or benign.

Water is used as a chemical feedstock for hydrogen production and as a coolant for the production process. Process and cooling water must meet minimum quality specifications (limits on mineral and organic contaminants) at both the inlet to the process and at the point of discharge. If these specifications are not met, then the water must be treated, which involves extra expenditure on equipment and energy. Furthermore, there are multiple options for water treatment and cooling systems, each of which has a different profile of equipment cost and operational requirements. The engineering decisions that are made when building out the hydrogen infrastructure will play an important role in the cost of producing hydrogen, and those decisions will be influenced by the regional and national policies that help to manage water resources.

Approach

In order to evaluate the impacts of water on hydrogen production and of a hydrogen economy on water resources, this project takes a narrowly-scoped lifecycle analysis approach. We begin with a process model of hydrogen production and calculate the process water, cooling, electricity and energy feedstock demands. We expand beyond the production process itself by analyzing the details of the cooling system and water treatment system. At a regional scale, we also consider the water use associated with the electricity and fuel that feed hydrogen production and distribution.

The narrow scope of the lifecycle analysis enables economic optimization at the plant level with respect to cooling and water treatment technologies. As water withdrawal and disposal costs increase, more expensive, but more water-efficient technologies become more attractive. Some of the benefits of these technologies are offset by their increased energy usage. We use the H2A hydrogen production model to determine the overall cost of hydrogen under a range of water cost and technology scenarios.

At the regional level, we are planning on following the hydrogen roll-out scenarios envisioned by Greene and Leiby (2008) [1] to determine the impact of hydrogen market penetration on various watersheds. The economics of various water technologies will eventually be incorporated into the temporal and geographic MSM via a water module that automates the spreadsheet models described above.

Results

At the time of this progress report, the major achievement for Fiscal Year 2009 has been the completion of the framework and analytical results of the economic optimization of water technology for hydrogen production. This accomplishment required

the collection of cost and performance data for multiple cooling and water treatment technologies, as well as the integration of a water and energy balance model with the H2A framework.

Twenty-two different combinations of production method (SMR, electrolysis), scale (centralized, forecourt), cooling (evaporative tower, dry) and water treatment (reverse osmosis, ion exchange) were evaluated. The following data were collected: water withdrawal, water discharge, electricity consumption, equipment footprint, equipment cost, installation cost, annual equipment and material costs and annual labor costs. These data, when consolidated, fit into a small number of input cells in H2A. Items such as capital cost end up as line-items for which there is space in the existing H2A spreadsheets. Items such as electricity use are added to the values that already exist in H2A.

Table 1 lists eight potential technology combinations for cooling and water treatment associated with centralized SMR hydrogen production. When water costs are very low, the most economical system is described by row B, however, as water purchase and discharge prices rise, systems with higher water efficiency prevail. Tables 2a, 2b and 2c show the price of hydrogen production as a function of water purchase and discharge price. In Table 2a, the technology is fixed. In Table 2b, the price is the lowest of the eight available water technology options. Table 2c identifies the chosen technology for the economic conditions.

TABLE 1. Cooling and Water Treatment Technologies for Central SMR Hydrogen Production

Treatment Systems Analyzed			
	Cooling Technology	Water Treatment Technology	Water Discharge
A	Cooling Tower	Ion Exchange	Zero
B	Cooling Tower	Reverse Osmosis	Minimal
C	Cooling Tower	Ion Exchange	Conventional
D	Cooling Tower	Reverse Osmosis	Conventional
E	Air Cooling	Ion Exchange	Zero
F	Air Cooling	Reverse Osmosis	Minimal
G	Air Cooling	Ion Exchange	Conventional
H	Air Cooling	Reverse Osmosis	Conventional

As can be seen from comparison of Tables 2b and 2c, in cases of extreme water strain (very high water purchase or discharge prices) the savings resulting from advanced treatment and cooling technologies can be significant. However, it is worth noting that such high water prices are exceedingly rare at this time.

TABLE 2A. Hydrogen Costs vs. Water Purchase and Discharge Costs – Fixed Technology

		Purchase Price for Water (\$/gal)				
		\$0.0001	\$0.001	\$0.01	\$0.10	\$1.00
Discharge Price for Waste Water (\$/gal)	\$0.0001	\$1.359	\$1.364	\$1.417	\$1.944	\$7.211
	\$0.001	\$1.360	\$1.365	\$1.418	\$1.945	\$7.212
	\$0.01	\$1.372	\$1.377	\$1.430	\$1.956	\$7.224
	\$0.10	\$1.487	\$1.492	\$1.545	\$2.072	\$7.340
	\$1.00	\$2.643	\$2.649	\$2.701	\$3.228	\$8.496

TABLE 2B. Hydrogen Costs vs. Water Purchase and Discharge Costs – Optimum Technology

		Purchase Price for Water (\$/gal)				
		\$0.0001	\$0.001	\$0.01	\$0.10	\$1.00
Discharge Price for Waste Water (\$/gal)	\$0.0001	1.359	1.364	1.414	1.668	3.717
	\$0.001	1.360	1.365	1.415	1.669	3.717
	\$0.01	1.372	1.377	1.425	1.678	3.717
	\$0.10	1.487	1.492	1.520	1.773	3.717
	\$1.00	1.957	1.959	1.975	2.133	3.717

TABLE 2C. Optimum Technology vs. Water Purchase and Discharge Costs

		Purchase Price for Water (\$/gal)				
		\$0.0001	\$0.001	\$0.01	\$0.10	\$1.00
Discharge Price for Waste Water (\$/gal)	\$0.0001	B	B	F	F	E
	\$0.001	B	B	F	F	E
	\$0.01	B	B	F	F	E
	\$0.10	B	B	F	F	E
	\$1.00	E	E	E	E	E

See Table 1 for definition of letters.

Conclusions and Future Directions

This analysis has shown that at current prices, water is not expected to have a major impact on hydrogen deployment. In previous years' work, it was shown qualitatively that acquisition of water rights (permitting) can present a major issue for any new water user, particularly in highly water stressed areas. However, because water rights are complex and contentious, further quantitative analysis of this hurdle was not pursued. Instead, a methodology for placing an upper bound on hydrogen price with respect to water (i.e. minimization of water use and discharge through advanced technology) was developed. This methodology resulted in the economic optimization described above.

In the remaining months of this project, the following tasks will be completed:

- Calculate regional water impacts over time with the projected hydrogen rollout scenarios proposed by Green and Lieby (2008) [1].
- Work with SNL to incorporate SNL's model of national and regional water resources with hydrogen rollout scenarios.
- Work with NREL and SNL to incorporate water analysis into the MSM.

FY 2009 Publications/Presentations

1. Simon, A.J. "Water's Role in a Hydrogen Economy", presentation to the Fuel Pathways Integration Technical Team (FPITT), March 18, 2009. Washington, DC.
2. Simon, A.J., "Water's Impacts on Hydrogen", presentation to the DOE's Annual Merit Review, May 19, 2009. Alexandria, VA.

References

1. Greene, D.L et. al. "Analysis of the Transition to Hydrogen Fuel Cell Vehicles and the Potential Hydrogen Energy Infrastructure Requirements." Oak Ridge National Laboratory, March 2008.
2. White, R.G. "Water Needs and Constraints for Hydrogen Pathways" part of the 2008 DOE Hydrogen Technologies Annual Progress Report.

VII.3 Cost Implications of Hydrogen Quality Requirements

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Project Start Date: October 01, 2005
Project End Date: September 30, 2015

Objectives

The objective of this project is to correlate the impurity concentrations in hydrogen dispensed at refueling centers to the cost of that hydrogen. The relationship is a function of the:

- Hydrogen production pathways, e.g., natural gas steam reforming followed by pressure swing adsorption (PSA).
- Process design and operating parameters, such as the choice of sorbents in the PSA, the system pressure, and temperatures at various locations, etc.

Technical Barriers

This project addresses the following technical barriers from the Systems Analysis section (4.5) of the Hydrogen, Fuel Cells, and Infrastructure Technologies (HFCIT) Program Multi-Year Research, Development and Demonstration Plan:

- (B) Stove-piped/Siloed Analytical Capability
 - Segmented Resources
- (A) Suite of Models and Tools
 - Macro-System Models

Contribution to Achievement of DOE Systems Analysis Milestones

This project will contribute to achieving the following DOE Systems Analysis milestones from the Systems Analysis section of the Hydrogen, Fuel Cells, and Infrastructure Technologies Program Multi-Year Research, Development, and Demonstration Plan:

- **Milestone 5:** *Complete analysis and studies of resource/feedstock, production/delivery and existing infrastructure for various hydrogen scenarios. (4Q, 2009)* Different hydrogen production and dispensing scenarios potentially entail different contaminants at different concentrations. In the current phase of our analyses, we have quantified the key fuel contaminants in three hydrogen production scenarios.
- **Milestone 6:** *Complete analysis of the impact of hydrogen quality on the hydrogen production cost and the fuel cell performance. (4Q, 2010)* We are developing models for the effects of contaminants on the performance and costs of hydrogen production and purification, and for the degradation in the performance and durability of fuel cell systems. These models will permit trade-off and sensitivity analyses of these effects on a life-cycle cost basis.
- **Milestone 9:** *Complete analysis of the impact of hydrogen quality on the hydrogen production cost and the fuel cell performance for the long range technologies and technology readiness. (2Q, 2015)* Analyses similar to the ones described here will be extended to longer term technologies for hydrogen production, purification, use in the fuel cells, and hydrogen analysis and quality verification as those technologies reach a suitable stage of development for such analyses.

Accomplishments

- A detailed component model (using Comsol Multiphysics) of the PSA process has been set up as part of a flexible MATLAB-based systems model.
- The hydrogen production pathway for natural gas steam reforming (NG-SR) followed by PSA has been studied over a broad range of key design and operating parameters.
- The system model results have been used to calculate the cost of hydrogen using H₂A for the NG-SR-PSA pathway. These results were used to plot the cost of hydrogen vs. impurity concentrations.
- A process model has been set up for the autothermal reforming of natural gas followed by PSA. Some preliminary calculations have been done for a coal gasifier followed by a PSA.

Introduction

Developing and implementing fuel quality specifications for hydrogen are a prerequisite to the widespread deployment of hydrogen-fueled fuel cell vehicles. Several organizations are addressing this fuel quality issue, including the International Organization for Standardization (ISO), the Society of Automotive Engineers (SAE), the California Fuel Cell Partnership, and the New Energy and Industrial Technology Development Organization/Japan Automobile Research Institute, and DOE's research projects at the national laboratories (Argonne National Laboratory, Los Alamos National Laboratory, Savannah River National Laboratory) and universities (Hawaii Natural Energy Institute, University of South Carolina, University of Connecticut, and Clemson University). These activities have focused on the deleterious effects of different potential contaminant on the automotive fuel cell or on-board hydrogen storage systems.

While it is possible to provide extremely pure hydrogen to the fuel cell vehicle, the production, purification, delivery and dispensing costs determine the type and concentration of the impurity or contaminant initially present when the hydrogen is generated by a given production pathway. It is the objective of this task to study the effect of the production pathway and the choice of process (design and operating) parameters on the impurity concentrations in and, ultimately, the cost of, the dispensed hydrogen.

The distributed production of hydrogen (for a system capable of producing 1,500 kg H₂ per day) based on the SR of NG and followed by purification using the PSA process has been identified as the most likely near-term solution for refueling fuel cell vehicles. Therefore, this pathway was the first to be modeled and studied, and some of the results are included in this report.

Approach

The cost of hydrogen is dependent on many factors at the various stages in the production pathway. It begins with (1) the feedstock that is used for its production, e.g., NG, water, coal, etc., followed by (2) the conversion of the feedstock, e.g., SR, electrolysis, gasification, etc., followed by (3) the purification of the hydrogen produced in the conversion step, e.g., PSA, hydrogen transport membranes, etc. Finally, (4) the cost of compression and delivery of the product hydrogen is determined by the pressures at which the hydrogen is available in step (3) and the storage pressure on-board the vehicle.

This project is assessing the cost of the product hydrogen by setting up a pathway model using MATLAB, which integrates the results of more detailed component models (e.g., for PSA) set up using Comsol Multiphysics. These models are then exercised to study the effect

of key process design and operating parameters on the performance measures such as process efficiency, concentrations of non-hydrogen species at various points in the process, hydrogen recovery in the PSA unit, etc. The process efficiency (for a particular set of conditions) calculated from our model can then be entered into the H2A spreadsheet, which contains the relevant assumptions for the financial calculations, to arrive at the cost (\$/kg) of hydrogen.

A final cost item is due to the composition analysis needed to ensure that the product hydrogen meets the regulatory quality standards (yet to be established). In consideration of the highly specialized analysis that is needed for the trace levels of some contaminants (e.g., ammonia and sulfur), some preliminary cost estimates have been published [1].

Results

The process models have been set up for three production pathways during Fiscal Year 2009. The NG-SR-PSA process was the first studied and is shown in Figure 1, where the process conditions are specified for the reference or "base" case. The NG, assumed to be available at the plant gate at 3 atm absolute pressure, is compressed to the process pressure (the reformer, shift reactor, and the PSA are assumed to operate at the same pressure) before it reacts with steam in the reformer. For the base case, the reformat exits the reformer and the shift reactors at 750°C and 435°C, respectively. The reformat enters the PSA at 25°C containing 76.5% hydrogen, 2.8% CO, 0.4% N₂, 2.8% CH₄, and 17.5% CO₂. The product hydrogen from the PSA is then compressed to the final delivery pressure of 430 atm. The tail gas from the PSA, which contains the impurities (CO₂, CO, CH₄, N₂) as well as significant amounts of H₂, is burned to generate the heat for the reforming process.

The model is set up to track up to nine species through the pathway, including inerts (N₂, Ar, He), H₂S, and NH₃. Helium passes through the process unreacted, although its concentration in the final product hydrogen is diluted considerably, as shown in Figure 2 for the process conditions shown in the figure. The H₂S and NH₃ are removed very effectively by the sorbents in the PSA – their concentrations in the final product are calculated to be considerably lower than 10⁻¹²%. Under the base case set of conditions, the two species with the highest concentrations in the product hydrogen are N₂ and CO. Figure 3 (top) plots their concentrations in parts per million (ppm) as a function of the hydrogen recovery, which is defined as the molar flow of purified hydrogen in the product as a percentage of the molar flow of hydrogen entering the PSA unit. At a recovery of 74% the concentrations of CO and N₂ are 0.2 and 10 ppm, respectively, and meet the guideline values suggested by ISO and SAE. At higher recoveries, the CO concentration exceeds the recommended 0.2 ppm,

FIGURE 1. Schematic of the SMR-PSA System (Base Case)

FIGURE 2. The concentration of helium in natural gas gets diluted in the product hydrogen.

even though all the other contaminant species are at concentrations below the ISO/SAE suggested limits. Thus CO can be referred to as the (recovery-) limiting species. The plot at the bottom shows the efficiency of the process (at a steam-to-carbon ratio of 4) at the base case conditions to be approximately 66%, where the efficiency [1] is defined as the lower heating value (LHV) of the purified product hydrogen leaving the PSA unit as a percentage of the LHV of the natural gas entering the system. The electrical energy requirement (e.g., compression) are calculated and then entered into the H2A spreadsheet.

FIGURE 3. A CO specification of 0.2 ppm limits the H₂ recovery to 74% and the efficiency to ~66%.

The effect of several process parameters on performance (efficiency, impurity concentrations, etc.) have been studied for the NG-SR-PSA system described in Figure 1. These include the effect of the steam-to-carbon molar ratio, the effect of pressure, the effect of the PSA inlet temperature, and the effect of the proportion of carbon in the PSA beds. For example, a bed with 80% carbon (and 20% Zeolite) is much more

FIGURE 4. Hydrogen cost is a weak function of CO concentration (based on NG price of \$7.6/1,000 ft³ or \$7.8/MMBTU)

effective in removing methane, while a bed with 20% carbon (80% Zeolite) is more effective in removing CO. Our models calculated the process efficiency for each set of process conditions. Entering them into DOE's H2A spreadsheet generated the corresponding cost of hydrogen. These cost results are plotted in Figure 4, which shows the cost of hydrogen (\$/kg) vs. the concentration of CO in the hydrogen. Each subplot shows the effect of a different parameter. The curves in the figure show that there is a significant effect of these parameters on the cost of hydrogen. However, the cost is only slightly affected by the change in the CO concentration in the hydrogen. Reducing the CO from 10 to 0.1 ppm shows a difference of 3 cents in the cost per kg of hydrogen. The parametric sensitivity studies were conducted by changing only one variable at a time and did not attempt to optimize the parameters with respect to any objective function. The results presented in the figures are more significant with respect to the trends (slopes), rather than the absolute values (\$/kg).

Two other models have also been set up for analysis. These are for the (1) autothermal reforming of NG followed by hydrogen purification using PSA, and (2) coal gasification followed by PSA. Preliminary results indicate that the hydrogen recoveries in the PSA will likely be limited by the inerts (N₂, Ar) that are introduced with the oxygen (from air) for these two hydrogen production pathways.

Conclusions and Future Directions

A process model was set up and used to correlate the cost of hydrogen with the impurity concentrations in the product hydrogen. The pathway consisting of natural gas steam reforming followed by the PSA process was studied, to generate a series of plots of the cost of hydrogen vs. the concentrations of impurities (N₂, CO, etc.) as functions of the key process parameters. The results showed that,

- For the NG-SR-PSA pathway, the cost of hydrogen is only slightly affected by the impurity concentration for given process conditions. Changing the key process parameters, however, can lead to sharp changes in the cost of hydrogen. There are significant opportunities for optimization of the plant.
- For most conditions in the NG-SR-PSA pathway, the CO specification limits the hydrogen recovery. Nitrogen may become the limiting species in certain cases, such as when the beds are loaded with high zeolite content, or when the natural gas feedstock contains high concentrations of nitrogen.
- Helium present in the natural gas will pass through the NG-SR-PSA process and will emerge in the product hydrogen, but at about one-fourth the concentration in the feed natural gas. Helium has a suggested 300 ppm upper limit in the product H₂; thus, any NG that contains 1,200 ppm or more of

helium would be unsuitable for producing H₂ for fuel cell vehicles.

- For the autothermal reforming (ATR) of NG followed by PSA purification, the Ar or N₂ specification may limit the maximum H₂ recovery achievable in the PSA.
- Similarly, for coal gas reforming followed by PSA, the H₂ recovery may be limited by the Ar or the N₂ specification.

For the future, we will:

- Evaluate the impurity concentrations likely from other hydrogen production pathways such as ATR, coal gasification, electrolysis.
- Validate the NG-SR model results with field data.
- Incorporate more complex PSA systems if needed.
- Incorporate our model results into H2A.

FY 2009 Publications/Presentations

1. D. Papadimas, S. Ahmed, R. Kumar, X. Wang, R.K. Ahluwalia, "Update on Hydrogen Quality: Modeling the Reformer/PSA System and Effect of H₂S on Fuel Cell Performance," presented to the Fuel Cell TT and Codes & Standards TT, Southfield, MI, August 2008.
2. Joseck, F., Papadimas, D., Ahmed, S., R. Kumar, "Fuel Quality Impacts on Hydrogen Production, Purification and Use in Fuel Cell Automobiles," 2008 Fuel Cell Seminar, Phoenix, AZ, October, 2008.
3. D. Papadimas, S. Ahmed, R. Kumar, "Modeling a Hydrogen Production Pathway – Natural Gas Steam Reforming followed by Pressure Swing Adsorption," presented at the Modeling Workshop, Golden, CO, November, 2008.
4. D. Papadimas, S. Ahmed, R. Kumar, F. Joseck, "Hydrogen Quality for Fuel Cell Vehicles – A Modeling Study of the Sensitivity of Impurity Content in Hydrogen to the Process Variables in the SMR-PSA Pathway," accepted for publication, International Journal of Hydrogen Energy, 2009.
5. R. Kumar, D. Papadimas, S. Ahmed, "Hydrogen Quality for Fuel Cell Vehicles," presented to the FreedomCar Joint Operations Group, December, 2008.
6. S. Ahmed, D. Papadimas, R. Kumar, "Modeling a Hydrogen Production Pathway – Natural Gas Reforming followed by Pressure Swing Adsorption," presented at the ISO-WG12 Meeting, Grenoble, France, February, 2009.

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1. D. Papadimas, S. Ahmed, R. Kumar, F. Joseck, "Hydrogen Quality for Fuel Cell Vehicles – A Modeling Study of the Sensitivity of Impurity Content in Hydrogen to the Process Variables in the SMR-PSA Pathway," accepted for publication, International Journal of Hydrogen Energy, 2009.

VII.4 Macro-System Model

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Project Start Date: February 7, 2005
Project End Date: September 30, 2010

Objectives

Develop a macro-system model (MSM) aimed at:

- Performing rapid cross-cutting analysis.
- Utilizing and linking other models.
- Improving consistency of technology representation (i.e., consistency between models).
- Supporting decisions regarding programmatic investments and focus of funding through analyses and sensitivity runs.
- Supporting estimates of program outputs and outcomes.

2008/2009 objectives:

- Improve the structure of the MSM and expand the graphics user interface (GUI).
- Update versions of component models.
- Enhance stochastic analysis capability.
- Validate MSM results.
- Develop interactions between the MSM and spatial and temporal models.

Technical Barriers

This project addresses the following technical barriers from the Systems Analysis section of the Hydrogen, Fuel Cells and Infrastructure Technologies

Program Multi-Year Research, Development and Demonstration Plan:

- (B) Stove-Piped/Siloed Analytical Capabilities
- (C) Inconsistent Data, Assumptions, and Guidelines
- (D) Suite of Models and Tools

Contribution to Achievement of DOE Systems Analysis Milestones

This project contributes to achievement of the following DOE milestones from the Systems Analysis section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- **Milestone 5:** Complete analysis and studies of resource/feedstock, production/delivery and existing infrastructure for various hydrogen scenarios. (4Q, 2009)
- **Milestone 6:** Complete analysis of the impact of hydrogen quality on the hydrogen production cost and the fuel cell performance. (4Q, 2010)
- **Milestone 14:** Complete input/output guidelines for the Macro-System Model. (3Q, 2005)
- **Milestone 15:** Select model for analysis and incorporate into Macro-System Model. (4Q, 2005)
- **Milestone 16:** Develop initial model architecture. (4Q, 2005)
- **Milestone 17:** Capture Macro-System Model requirements, description, and usage in a description document. (2Q, 2006)
- **Milestone 18:** Complete a usable “test version” of the Macro-System Model with links to the H2A Production and Delivery models and the ANL GREET model. (2Q, 2006)
- **Milestone 23:** Complete the 1st version of the Macro-System Model for the analysis of the hydrogen fuel infrastructure to support the transportation systems. (4Q, 2008)
- **Milestone 27:** Complete the 2nd version of the Macro-System Model to include the analytical capabilities to evaluate the electrical infrastructure. (2Q, 2011)

Accomplishments

- Completed Version 1.0 of the MSM and used it for programmatic analysis.
- Linked H2A Production cases with the Hydrogen Delivery Scenario Analysis Model (HDSAM), the Greenhouse Gases, Regulated Emissions, and Energy Use in Transportation (GREET) Model, and

physical property information from the Hydrogen Analysis Resource Center (HyARC) and validated the use of those models and the results generated using them.

- Developed a flexible, comprehensive Web-based user interface so that many members of the analysis community can use the MSM.
- Completed a User Guide for the MSM.
- Added stochastic (Monte Carlo) capabilities to the MSM.
- Upgraded the MSM to the latest versions of H2A Production (V.2.1), HDSAM (V 2.0) and GREET (V 1.8b).
- Initiated interaction with the geo-spatial model HyDRA to add the spatial dimension to the MSM. Currently, some of the MSM results are available in HyDRA.

Introduction

At the DOE Hydrogen Program's behest, we are developing a macro-system model to analyze cross-cutting issues because no existing model sufficiently simulates the entire system including feedstock, conversion, infrastructure, and vehicles with the necessary level of technical detail. In addition, development of the MSM exposes inconsistencies in methodologies and assumptions between different component models so that they can be identified and corrected when necessary.

Version 1.0 of the MSM has been developed and is available to the hydrogen analysis community. It links H2A Production, HDSAM, GREET, and physical property information from HyARC to estimate the economics, primary energy source requirements, and emissions of multiple hydrogen production/delivery pathways. A Web-based user interface has been developed so that many users have access to the MSM; stochastic capabilities have been added to it to provide uncertainty ranges around the results. The MSM has been used for several analyses to compare pathways and to understand the effects of varying parameters on pathway results.

Approach

The MSM is being developed as a tool that links or federates existing models across multiple platforms. This approach was chosen because the task of building a single monolithic model incorporating all of the relevant information in the existing models would have been overwhelming, as the necessary expertise to do so was spread among half a dozen DOE laboratories and a dozen or more universities and private contractors.

Linking models allows model users that depend on data from component models to continue using their models while retrieving data from component models in a less labor-intensive manner. In addition, it provides common platform for data exchange necessary to update integrated models when component models have been updated.

The MSM is being built on a framework inspired by the federated object model (FOM). FOMs also link together models and are exemplified by the Department of Defense High Level Architecture (HLA) [1]. The general MSM framework provides a common interlingua that is extensible (accommodates new models with a minimum of difficulty), distributable (can be used by multiple people in different areas of the country), and scalable (to large numbers of participating models). Version 1.0 of the MSM uses Ruby and Ruby interfaces to Microsoft Excel and other platforms to collect, transfer, and calculate data.

Results

Levelized hydrogen costs, primary energy requirements, and emissions have been estimated for multiple pathways using H2A 2.1, HDSAM V2.0, and GREET V1.8b. Figure 1 shows results for production of hydrogen from woody biomass via gasification in central plants using current technology followed by liquefaction and delivery of liquid hydrogen in trucks. To distribute 116,000 Btu of hydrogen (lower heating value – similar to the energy in one gallon of gasoline and 1.02 kg hydrogen), 129,000 Btu of hydrogen need to be produced – 13,000 Btu are lost due to unrecovered boil-off. In addition, 33,000 Btu of electricity are necessary to liquefy the hydrogen; 1,000 Btu of diesel fuel to transport the hydrogen; and 1,000 Btu to compress the hydrogen that has been revaporized so it can be dispensed to vehicles. To produce the necessary hydrogen, energy sources (biomass, electricity, and natural gas) are required as shown in the figure. The levelized cost at the pump for this pathway is estimated to be \$5.00/kg. That levelized cost is similar to that reported in the 2006 Hydrogen Posture Plan which was \$5.10/kg [2]. The difference is primarily due to liquefaction efficiency as calculated by HDSAM.

Because the MSM is a conjunction of several models, it can potentially involve variables present in each of the constituent models. Thus the total number of MSM input parameters can significantly exceed the number of inputs for an individual model and the user needs a compact and user-friendly way of accessing large number of variables. To fulfill that need, a 'branch and leaf' structure has been adopted. The input variables are grouped into blocks (each block representing a branch containing other blocks or input parameters) as shown in the example in Figure 2. In addition, this compact

FIGURE 1. Pathway Results for Central Hydrogen Production from Woody Biomass with Liquid Hydrogen Delivered by Trucks

FIGURE 2. Branched structure allows user access to virtually all input MSM parameters. In this example, the user modifies total capital investment for the production facility.

user interface excludes user access to parameters that are irrelevant to the pathway of interest.

Since model estimates have some variability, stochastic modeling capability in the form of Monte Carlo analysis has been added to the MSM. Stochastic tools available in the MSM include the DAKOTA toolbox [3] and @Risk. The latter was used in the MSM to characterize potential impact of greenhouse gas (GHG) emissions from transportation on fuel cost (gasoline vs. hydrogen produced by steam methane reforming at the refueling station). The input distributions (capital investment, operating and maintenance costs, production capacity factor, production unit efficiency) were largely taken from the program's uncertainty analysis [4] with the notable exception of gasoline and natural gas cost distributions which were based on historic data. A GHG emissions tax was applied to both the gasoline and hydrogen fuels at the level of \$50 per ton CO₂ equivalent. It increases the per mile cost of each fuel but the increase to gasoline exceeds that of hydrogen on average by a factor of 1.6 and incorporation of the GHG tax increases differentiation between hydrogen and gasoline. The results of this study are presented in Figure 3 in the form of a scatter plot.

Key MSM inputs are sometimes region-specific; therefore, key results are often region-specific as well. For this reason it is important to add the geo-spatial dimension to the MSM so we are linking the MSM to HyDRA - a set of tools for visualization and analysis of geographically distributed data. One example of a HyDRA link is the cost and associated GHG emission distributions for hydrogen produced from electrolysis.

FIGURE 3. Uncertainty analysis: the potential effect of transportation GHG emissions tax on fuel costs. Gasoline and hydrogen costs are shown in \$/mile of vehicle travel. The solid red line shows the equivalence level, the arrow denotes typical tax effect on data-point location.

HyDRA databases provided electricity cost and grid mix distributions and the MSM was run to generate levelized hydrogen cost and GHG emissions for each region. Those results identify two areas with both low hydrogen production cost (less than \$6/kg) and low associated emissions (not exceeding 550 g per mile vehicle travel). The two areas include a large region covering parts of Idaho, Oregon and Washington and a smaller shore region in Maine. The authors will provide the map imaging these two regions upon request.

Conclusions and Future Directions

Version 1.0 of the MSM has been developed to compare the economics, primary energy source requirements, and emissions of different hydrogen production/delivery pathways and is being used for comparative and sensitivity analyses. The MSM helps identify cost and environmental tradeoffs within and between pathways. Stochastic capability has been incorporated to improve nuance in results and a Web-based GUI has been employed so many members of the hydrogen analysis community can perform their own analyses.

The next steps for the MSM involve:

- Updating the MSM interaction with component models as they are released.
- Establishing direct links between geographical tools and the MSM.
- Linking at least one transition-scenario model to the MSM.
- Using the MSM to update production and delivery information for other models.
- Adding the combined heat, power, and hydrogen production pathway to the MSM.

FY 2009 Publications/Presentations

1. Ruth, M., Diakov, V., Goldsby, M., Sa, T. Macro-System Model: a Federated Object Model for Cross-Cutting Analysis of Hydrogen Production, Delivery, Consumption and Associated Emissions. In Winter Simulation Conference, 2009 (accepted for publication).
2. Ruth, M., Diakov, V., Sa, T., Goldsby, M., Genung, K., Hoseley, R., Smith, A., and Yuzugullu, E. 2009. Hydrogen macro-system model user guide. *Technical Report NREL/TP-6A1-44799*. Available via <http://www.nrel.gov/docs/fy09osti/44799.pdf>.

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VII.5 Discrete Choice Analysis of Consumer Preferences for Refueling Availability

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Project Start Date: September 1, 2007

Project End Date: May 28, 2009

- **Milestone 3:** Begin a coordinated study of market transformation analysis with H2A and Delivery Models. (1Q, 2006)

Accomplishments

- Redesigned and enhanced the discrete choice survey tool developed in Fiscal Year 2008.
- Fielded the improved survey in four metropolitan areas (Los Angeles, CA; Seattle, WA; Atlanta, GA; and Minneapolis-St. Paul, MN) and attained stated consumer preference data for refueling availability on three geographic scales: metropolitan, regional, and national (along interstates connecting major urban areas).
- Analyzed survey results and determined utility functions and associated cost penalties for limited refueling availability on an equivalent basis as the purchase price of a new vehicle.
- Quantified cost penalties associated with limited refueling availability for each geographic scale and identified general trends among each of the four metropolitan areas.

Objectives

- Quantify consumer reluctance to purchase an alternative fuel vehicle due to a lack of refueling availability.
- Compare survey results to comparable results derived from analytic models.
- Develop a general discrete choice model for major urban areas.

Technical Barriers

This project addresses the following technical barriers from the Systems Analysis section (4.5) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) Future Market Behavior
- (D) Suite of Models and Tools

Contribution to Achievement of DOE Systems Analysis Milestones

This project contributed to the achievement of the following DOE milestones from the Systems Analysis section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

Introduction

A lack of convenient refueling availability can be a significant deterrent to household consumers considering the purchase of a hydrogen vehicle. Several studies have developed estimates of the number of stations that may be needed to satisfy the refueling availability requirements of early adopters, but only a limited number of studies have attempted to quantify the consumer value, or disincentive, associated with limited refueling availability. This study involves an analysis of consumer responses to a hypothetical vehicle purchase decision posed through a detailed survey tool. The focus of this analysis is to develop representative cost penalties associated with different levels and geographic scales (metropolitan, regional, and national) of limited refueling availability.

The coordination of station and vehicle introductions over time (and space) determines the degree of infrastructure utilization, and therefore significantly influences fuel costs. Understanding the role of consumer preferences for refueling availability in the decision to purchase a hydrogen vehicle can therefore help to inform DOE technical targets related to the cost of hydrogen fuel.

Approach

Discrete choice analysis methods are commonly employed to quantify consumer preferences for similar products with distinct attributes, such as cost, performance, and appearance. In this study, a discrete choice survey tool was used to present a representative panel of households with a hypothetical choice to purchase one of two vehicles: a conventional vehicle and an alternative fuel vehicle (AFV). In choosing which vehicle they would prefer, the respondents took into consideration quantitative descriptions of vehicle attributes such as cost and range, as well as quantitative and visual representations of different levels and geographic scales of refueling availability. In the survey, the AFV was described as being identical to the conventional gasoline vehicle in all respects except two: (1) refueling availability might be more limited, and (2) the AFV would offer significant social and environmental benefits. The AFV was not associated with any particular alternative fuel.

A series of initial screening questions collected information about the participant's driving behavior and acquainted him or her with the setup of the survey, the definitions used to describe vehicle attributes, and the maps used to represent refueling availability on three geographic scales: metropolitan, regional, and nationwide along interstate highways connecting major cities. For example, the "level 2" coverage map used for the Seattle metropolitan area is shown in Figure 1. The corresponding Seattle level 1 indicates fewer stations, level 3 indicates more stations, and the level 4 map indicates equivalent coverage as conventional gasoline

FIGURE 1. Survey Map Example: Metropolitan Coverage for Seattle, WA

stations. Similar maps were used to indicate four levels of refueling availability on regional and nationwide geographic scales. Consumer responsiveness to vehicle purchase price was used to normalize responsiveness to levels of refueling availability, allowing for the determination of cost penalties on an equivalent basis as the purchase price of a new vehicle.

Results

The 2009 survey results are an improvement over the 2008 survey results. By comparison, utility functions based upon the 2009 survey data have a moderately increased level of predictive power, include a larger number of statistically significant parameters, and provide more consistent penalty estimates within policy-relevant ranges of refueling availability. These improvements are at least partly due to the improved 2009 survey design, which included more realistic map images, a simplified set of choice task attributes (focusing on refueling coverage and vehicle purchase price), and improved sets of coverage attribute levels (e.g., metro area coverage levels 1 and 2 are more distinct, and level 1 regional coverage is changed from zero to a small number of stations). Cost penalty results associated with metropolitan area coverage are comparable to those found in other discrete choice studies [1-4], and are higher than results from analytic studies based upon "rational" economic models of consumer behavior [5,6]. The metro penalties are significantly lower than those determined from the 2008 survey, and, unlike the 2008 results, the ordering of the cost penalties does not correspond to metro area population density. A new contribution to the literature, from both the 2008 and 2009 studies, is estimation of cost penalties for regional and national geographies. The national penalties from the 2009 survey are slightly higher than those from the 2008 survey, and the regional penalties are comparable in magnitude to the 2008 results but have been captured in greater detail as a result of the improved 2009 survey.

Cost penalties associated with limited coverage on a metropolitan scale are indicated in Figure 2, where the horizontal axis indicates the percentage of existing gasoline stations in each metro area and the vertical axis is the equivalent vehicle purchase price cost penalty. Trend lines emphasize that cost penalties drop as a higher percentage of stations offer an alternative fuel. Penalties range from \$1,000 to \$3,000 at metro coverage levels below 5% of stations, and drop to between \$500 and \$2,000 near 10% of stations. Estimated penalties are less than \$500 beyond 30% of stations. Figure 3 indicates cost penalties for limited regional coverage, with the horizontal axis indicating the absolute number of stations located within 150 miles of the metropolitan area. Penalties range from \$2,000 to \$3,000 with 10 regional stations. Trend lines suggest that these penalties would drop to between \$1,000 and \$2,000 with

FIGURE 2. Cost Penalties For Metropolitan Coverage

FIGURE 3. Cost Penalties For Regional Coverage

approximately 100 regional stations; a modest reduction given the absolute increase in stations. Interestingly, and somewhat surprisingly, the trend lines shown approach zero close to the estimated total number of stations in each region [7]. Penalties for limited national coverage along interstates are indicated in Figure 4, with the horizontal axis indicating the number of long-distance trips between major U.S. urban areas that would not be viable from each city. The maximum interstate coverage penalties occur when 100% of long-distance trips are not viable (right-hand side of the horizontal axis). The basis of trip numbers between cities is determined using American Travel Survey data. As was the case with analysis of the 2008 survey results, national cost penalties are relatively high, with penalties of roughly \$2,500 to \$5,000 associated with the last 10% of long-distance trips not covered.

Conclusions and Future Direction

Significant cost penalties appear to be associated with limited refueling availability. The results of the present study are based upon stated preferences, which are more speculative than revealed preference data. Given that revealed preference data on this issue are sparse or non-existent, the survey results attained here do improve our understanding of consumer expectations

FIGURE 4. Cost Penalties For National Interstate Coverage

and perceptions of the value of refueling availability. Analysis results based upon the improved 2009 survey are consistent with the 2008 results in indicating that coverage on a regional scale (within 150 miles of the city center) and on a national scale (along interstates) appear to be as influential in the decision to purchase a vehicle as coverage within metropolitan areas. Relatively consistent trends were identified among the four cities, providing support for a generalized representation of refueling availability penalties for major urban areas. These results can be used in two potential future applications: (1) to enhance hydrogen infrastructure transition models that include a spatially detailed representations of refueling availability, and (2) to inform policies determining financial support for hydrogen vehicles and associated refueling infrastructure.

FY 2009 Publications/Presentations

1. PA Consulting Group, *Discrete Choice Analysis for Hydrogen Vehicles*. National Renewable Energy Laboratory, Golden, CO, subcontractor report. Forthcoming.
2. Melaina, M., "Hydrogen Infrastructure Analysis Highlights." Presented at the Institute of Transportation Studies, University of California Davis, May 4, 2009, Davis, CA.
3. Melaina, M., "Hydrogen Infrastructure Analysis Highlights. Presented at General Motors Powertrain," May 7, 2009, Pontiac, MI.
4. Melaina, M., "Discrete Choice Analysis of Consumer Preferences for Refueling Availability." Presented at the 2009 DOE Hydrogen Program Merit Review and Peer Evaluation Meeting, May 19, 2009, Washington, DC.
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VII.6 Analysis of Energy Infrastructures and Potential Impacts from an Emergent Hydrogen Fueling Infrastructure

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Project Start Date: December 1, 2007
Project End Date: September 30, 2012

Objectives

- Develop models of interdependent energy infrastructure systems.
- Analyze the impacts of widespread deployment of a hydrogen fueling infrastructure.
- Identify potential system-wide deficiencies that would hinder infrastructure growth.

Technical Barriers

This project addresses the following technical barriers from the Systems Analysis section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) Future Market Behavior
- (B) Stove-piped/Siloed Analytical Capability
- (E) Unplanned Studies and Analysis

Contribution to Achievement of DOE Systems Analysis Milestones

This project will contribute to achievement of the following DOE milestones from the Systems Analysis section of the Hydrogen, Fuel Cells and Infrastructure Technologies (HFCIT) Program Multi-Year Research, Development and Demonstration Plan:

- **Milestone 5:** Complete analysis and studies of resource/feedstock, production/delivery and existing infrastructure for various hydrogen scenarios. (4Q, 2009)

- **Milestone 7:** Analysis of the hydrogen infrastructure and technical target progress for the hydrogen fuel and vehicles. (2Q, 2011)
- **Milestone 8:** Complete analysis and studies of resource/feedstock, production/delivery and existing infrastructure for technology readiness. (4Q, 2014)

Accomplishments

- Sandia National Laboratories developed a dynamic tool for analyzing the potential impact of an emergent hydrogen fuel infrastructure on the existing energy infrastructures.
- Developed models of the market behavior of natural gas (NG), refined petroleum, hydrogen, and electricity generation in California (CA).
- Incorporated a vehicle adoption model based on the Struben and Sterman [1] formulation for hydrogen fuel cell vehicles (HFCVs) and plug-in hybrid electric vehicles (PHEVs).
- Performed analysis of vehicle penetration scenarios to project increased demand and prices for hydrogen, NG, and electricity.

Introduction

The HFCIT program envisions the transition to hydrogen vehicles will begin by taking advantage of the existing infrastructure for NG. Since hydrogen production by steam-methane reforming (SMR) is currently the most economical production pathway [2], we start with a study of the impact of hydrogen vehicles on demand for NG. Natural gas demand comes from several sectors, so growing demand from hydrogen production can potentially affect sectors such as electricity generation. Understanding the potential impacts of a hydrogen refueling infrastructure requires a model that couples the markets for natural gas and electricity.

In addition to hydrogen vehicles, PHEVs may provide an alternative to conventional gasoline vehicles. Competition between HFCVs and PHEVs will depend on their relative performance and cost, including the costs of hydrogen, electricity, NG, and gasoline.

Approach

We use the system dynamics approach to simulate the interaction of vehicle adoption and infrastructure

for hydrogen, electricity, NG, and gasoline. The model formulation considers vehicle sales to occur according to a driver's willingness-to-adopt the alternative vehicles, which is parameterized by factors for the effectiveness of advertising and word-of-mouth [1]. Given a willingness-to-adopt, drivers will purchase the alternative vehicles when the performance of the vehicle, measured here as an operating cost (per mile), favors the alternative. The performance relative to conventional vehicles depends on the incremental sales cost spread over the vehicle life, as well as the fuel cost and mileage. The assumptions for vehicle performance are listed in Table 1.

TABLE 1. Vehicle Model Assumptions

Gasoline vehicle mileage	20 mpg
PHEV	
Gasoline mileage	48 mpg
Electric mileage	0.35 kWh/mi
Fraction electric mode	2/3
Electric range	40 miles
HFCV Mileage	65 miles/kg
Total vehicle sales rate	6%/yr
Total vehicle scrap rate	5%/yr

The model considers the energy infrastructure for California, because the state is a “lighthouse” region expected to lead the way in adopting HFCVs. The infrastructure model computes fuel demand from the vehicles and balances this with supplies to estimate price variations. The model uses traditional elasticity parameters to represent the price of NG and refined gasoline, which for CA is a unique blend not available from out-of-state refiners. The gasoline price uses the projected oil price and adds a refining margin that varies with a supply elasticity. The demand for NG comes from electricity generation and vehicles, which couples these HFCVs and PHEVs, because the reformed hydrogen and the variable electricity demand both consume NG. The assumptions for the energy markets are listed in Table 2.

Results

The model simulates the market adoption of PHEVs and HFCVs to replace conventional gasoline vehicles in time. The parameters in the adoption model are adjusted to capture the vehicle sales fractions suggested by Scenario #1 of the Greene *et al* [3] study; we use this team's study of potential vehicle adoption as a reference case upon which to begin evaluating the impact of the vehicles on the infrastructure. A departure from Greene *et al* is that we substitute PHEVs for gasoline hybrids. Figure 1 shows the simulated number of vehicles on the road for this reference scenario. The PHEVs are adopted before the HFCVs, because the incremental cost

TABLE 2. Infrastructure Model Assumptions

Natural Gas	
Supply:	Imports and in-state production
Demand:	<ul style="list-style-type: none"> Electric generation H₂ demand from SMR Industrial, commercial, and residential are constant
Price:	<ul style="list-style-type: none"> Varies with market elasticity Initial value: \$8/GJ
Hydrogen	
Demand	HFCV
Price	<ul style="list-style-type: none"> Computed from NG price via SMR at 70% efficiency Includes \$1/kg fixed cost Initial value: \$3/kg
Electricity	
Supply:	<ul style="list-style-type: none"> Imports: 31% of total 54% of imports from coal Must-run generation: nuclear, hydro, other renewable Variable generation: NG
Demand:	<ul style="list-style-type: none"> Load data with hourly resolution (Cal-ISO over 1 yr, 2007) PHEV charging at night
Price:	<ul style="list-style-type: none"> Weighted average of fixed and variable generation costs Initial value: 12 ¢/kWh
Gasoline	
Supply:	Refinery capacity for CA compliant gasoline
Demand:	Conventional and PHEV consumption
Price:	<ul style="list-style-type: none"> Oil price rises linearly from \$65/bbl to \$140/bbl in 2030 Refining mSargin market elasticity Initial value: \$2.50/gallon

FIGURE 1. Number of PHEVs (dotted curve), HFCVs (solid curve), and total vehicles (dot-dashed curve) in California during the reference case simulation.

of the HFCVs includes an exponentially decaying cost per mile that makes the fuel cell vehicles too expensive until about 2020, consistent with the learning curve used by Greene *et al* [3].

The increasing demand for NG – from both PHEVs and HFCVs – causes the price to increase 150% by mid-century. Figure 2 shows the increase in price for the fuels during time, relative to the initial prices given in Table 2. The hydrogen price tracks the NG price, because SMR is the only path to hydrogen; however, the relative increase is not the same, because there is a fixed cost of \$1/kg added to the contribution from NG. The NG price increases by a larger fraction than electricity, because of the extra demand of the HFCV; note that this reference case holds the other electricity demand fixed at the 2007 level.

The gasoline price shows an interesting dynamic caused by the reduced demand. Despite the linearly increasing oil price, the gasoline price flattens out during the decade following 2020 due to the reduced refining margin. After the refining margin reaches a minimum, the price rises again with the assumed linearly increasing oil price. While this gasoline price reduction is plausible, the model may not be realistic at extremely low demand for gasoline, because the oil price would probably not continue to increase on the world market.

The dynamic model can be used to examine the effects of a variety of parameters. For example, what if the HFCVs do not achieve DOE HFCIT program targets? Decreasing the HFCV mileage to only 55 mile/kg means that PHEVs maintain a majority of market share by 2050. What if conventional vehicles increase their efficiency? Increasing the conventional vehicles over time to 30 mpg decreases the market adoption of PHEV in the near term, but the HFCVs are adopted at about the same rate in the longer term. What about the effect of a cost for carbon emissions? Imposing a carbon

FIGURE 2. Price change (in percent) from the beginning of the dynamic simulation for electricity (solid curve), NG (dashed curve), gasoline (dotted curve), and hydrogen (dot-dashed curve).

dioxide cost of \$200/tonne, which is about \$1.75/gallon of gasoline, increases the PHEVs on the road by about 4 million vehicles, because the electricity used by the PHEVs for two-thirds of their travel has lower average carbon emissions than gasoline. Interestingly, the simulation suggests about the same population of HFCVs as the reference case, because the carbon cost on the SMR path adds \$1.85/kg to the hydrogen price, but adds only 3 ¢/mile to the operating cost.

The dynamic model suggests that the most critical component of the CA energy infrastructure will be the capacity for importing NG. Figure 3 shows the fraction of the supply capacity that must be used to import the NG to meet demand under three scenarios. The reference scenario considers the increased adoption of vehicles only, without any growth in other electricity demand; this scenario suggests the existing import pipeline capacity will not be exceeded by mid-century – although operation at 95% of capacity will likely have problems supplying seasonal variations. However, the electric growth alone will likely stress the NG supply system much sooner; electric demand growth of 1% per year will exceed NG import capacity by 2035. Adding the reference case penetration of alternative vehicles exacerbates the NG supply problem by moving the critical point up about a decade.

Conclusions and Future Directions

The dynamic model for the CA energy markets predicts significant price increases for NG and electricity if an aggressive scenario of PHEV and HFCV adoption occurs. The coupling of plug-in and hydrogen vehicles supplied by SMR links both vehicles to the supply of NG. The simulations suggest that understanding the CA energy market in the coming decades requires predicting the supply and price of NG.

FIGURE 3. Fraction of the NG pipeline capacity necessary to import NG into California to meet demand for three cases: reference case for alternative vehicles only (solid curve); electricity growth at 1%/yr but without alternative vehicles (dotted curve); and the combination of electricity growth and alternative vehicles (dashed curve).

The plan for future work includes more dynamic modeling of the NG flows into the state and providing an electrolysis option for hydrogen production, coupled to increased renewable electricity to meet California's Renewable Portfolio Standard. Next year's work will focus on applying the influence of stationary fuel cell systems for production of electricity and hydrogen.

FY 2009 Publications/Presentations

1. MIT/Ford/Shell Research Workshop on Strategies for Market Transitions to Alternative Energy and Transportation Systems, Detroit, MI, June 9, 2009.
2. Fuel Pathways Integration Technology Team, Golden, CO, June 16, 2009.

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2. James, B and Perez, J, "Hydrogen Pathway Analysis using HyPro", DOE HFCIT Annual Merit Review, May 2007.
3. Greene, D., Leiby, P., James, B., Perez, J., Melendez, M., Milbrandt, A., Unnasch, S., Hooks, M., "Analysis of the Transition to Hydrogen Fuel Cell Vehicles and the Potential Hydrogen Energy Infrastructure Requirements", ORNL/TM-2008/30, March 2008.

VII.7 Hydrogen Deployment System Modeling Environment (HyDS-ME)

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Project Start Date: May 1, 2005

Project End Date: September 30, 2009

Contribution to Achievement of DOE Systems Analysis Milestones

This project will contribute to achievement of the following DOE milestones from the Systems Analysis section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- **Milestone 3.** Begin a coordinated study of market transformation analysis with H2A and Delivery models. (1Q, 2006)
- **Milestone 5.** Complete analysis and studies of resource/feedstock, production/delivery and existing infrastructure for various hydrogen scenarios. (4Q, 2009)
- **Milestone 8.** Complete analysis and studies of resource/feedstock, production/delivery and existing infrastructure for technology readiness. (4Q, 2014)
- **Milestone 24.** Complete the linear optimization model (HyDS) to analyze the optimum production facilities and infrastructure for hydrogen demand scenarios. (4Q, 2008)
- **Milestone 26.** Annual model update and validation. (4Q, 2008; 4Q, 2009; 4Q, 2010; 4Q, 2011; 4Q, 2012; 4Q, 2013; 4Q, 2014; 4Q, 2015)

Objectives

The Hydrogen Deployment System Modeling Environment (HyDS-ME) is a geospatially and temporally oriented analysis model that determines the optimal production and delivery scenarios for hydrogen, given resource availability and technology cost. The objects of the most recent phase of the project are:

- Evaluate the effectiveness of the HyDS-ME tool, design enhancements to it, and update the tool's capabilities.
- Perform several scenario analyses:
 - Exercise the enhanced tool on a notional case study.
 - Complete a study involving a mix of stationary and vehicular hydrogen uses.
- Expand the interoperability of HyDS-ME with tools such as HyDRA.

Technical Barriers

This project addresses the following technical barriers from the Systems Analysis section (4.5) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (B) Stove-piped/Siloed Analytical Capability
- (D) Suite of Models and Tools
- (E) Unplanned Studies and Analysis

Accomplishments

- Completed the HyDS-ME software updates, which involved the reworking of approximately 20k lines of code and the development of an enhanced architecture supporting open/interoperable data formats, increased flexibility/transparency, and faster optimization computations.
- Completed a notional California study documenting lessons learned regarding infrastructure optimization, insights into infrastructure tradeoffs, and insights into regional infrastructure.
- Improved the interoperability capabilities of HyDS-ME by providing generic connectivity via extensible markup language, geographic information systems (GIS), and relational databases in order to open future connectivity between it and the Macro-System Model, HyDRA, and other tools.
- Completed an exploratory national wind-hydrogen infrastructure study.

Introduction

The HyDS-ME fills a unique and important niche in the temporal and geospatial analysis of hydrogen infrastructure build-out for production and delivery [1-3]. It nicely complements other hydrogen analysis tools and is well suited to address the potential analysis scenarios involving the temporally specific geospatial deployment of hydrogen production and transmission infrastructure. Its key capabilities are (i) a semi-realistic optimization of physical build-out of hydrogen infrastructure, (ii) the unified treatment of production, transmission, and distribution, (iii) the ease with which new technologies can be added to an analysis, (iv) the consistent physical and economic computations, (v) the ability to estimate costs and cash flows, (vi) the spatial and temporal resolution of hydrogen infrastructure networks, (vii) regional specificity, and (viii) the allowance for exogenously specified urban hydrogen demands. Its internal architecture is flexible, and it is compatible with GIS and the H2A models [4,5].

HyDS-ME is designed to answer questions such as [6]:

- Which technologies will be used to provide hydrogen during infrastructure build-out?
- What synergies are there between cities and their distance to markets?
- How important and costly is it to serve rural areas?
- How can cities leverage one another's demand, thereby reducing cost and risk of stranded investments?
- Where can centralized versus onsite production technologies be most effective?
- How might external influences or policy constraints/incentives influence hydrogen infrastructure build-out?

Approach

In order to answer such questions, HyDS-ME supports analyses aimed at identifying optimal infrastructure to meet specified annual urban hydrogen demands, perhaps coupled to other multiple objectives and constraints. Cash flows are computed, detailed by infrastructure component, city, and region, and these provide insights into components of hydrogen costs, which are determined by year, volume, and locality. Three methods of long distance hydrogen transport are considered: pipeline, gaseous truck, and liquid truck. The major use of HyDS-ME is for studying potential turning points in infrastructure choice via sensitivity analysis on infrastructure, feedstock, and fuel cost inputs in the context of the complex transient and transitional interactions between increasing hydrogen demand and hydrogen infrastructure construction. With carefully constructed input data sets, HyDS-ME can also weigh tradeoffs between investments in various infrastructure types, given policy constraints (greenhouse gases, etc.).

Figure 1 shows the interrelationship between the input parameters for HyDS-ME and the algorithms applied to them in order to compute the delivered cost of hydrogen. The infrastructure networks are optimized using a simulated annealing algorithm that explores the large set of potential build-out plans that meet the input requirements for hydrogen delivery at cities over time. The hydrogen transport computations are based on graph-theoretic algorithms for determining optimal flows in networks. The cash flow computations rely on standard discounting approaches. Figure 2 shows an illustrative example of the geospatial results of hydrogen infrastructure optimization.

FIGURE 1. HyDS-ME Input and Output Data, And Algorithms

FIGURE 2. Geospatial layout of hydrogen infrastructure in example HyDS-ME optimization: blue circles represent steam methane reformer plants, green triangles electrolysis plants, red stars cities with hydrogen demand, red lines pipelines, and blue lines liquid truck transport.

Results

The most recent HyDS-ME notional case study involved studying the demand and feedstock sensitivities for hydrogen infrastructure build-out in California. Starting with canonical infrastructure, operating, and feedstock costs inferred from H2A models and demand profiles for California consistent with the 2008 National Academy of Sciences (NAS) scenarios [7], we develop a base case where infrastructure placement is optimized to reduce the total levelized production, transmission, and delivery costs for hydrogen. This results in localized hydrogen production (i.e., no long distance transport of hydrogen) with onsite production applications being the dominant method of providing hydrogen (see Figure 3). The consumption-weighted delivered hydrogen cost falls below \$10/kg in 2026 and below \$4/kg in 2032 in our base-case scenario, which roughly corresponds to the NAS “Hydrogen Success” scenario; in our scenario

FIGURE 3. Comparison of infrastructure build-out in the three NAS-inspired demand cases for a California case study.

FIGURE 4. Consumption-weighted delivered hydrogen costs for the three NAS-inspired demand scenarios.

corresponding to the NAS “Accelerated Hydrogen”, that cost falls below \$2/kg beyond 2030 (see Figure 4).

We also considered three simple scenarios involving the pricing of feedstocks for the onsite production technologies. The first two involve simply tripling or quadrupling the prices of the ethanol, natural gas, or electricity used by the three onsite technologies. The third involves assuming that feedstocks for those technologies are prohibitively expensive, so those

technologies are forbidden in the optimization. In effect these scenarios mimic the potential constraints (not modeled directly in HyDS-ME) that would limit the availability of feedstocks at points of onsite production within a city: the lack of sufficient distribution infrastructure (natural gas pipelines, electric power transmission lines, or ethanol transport) may increase the local feedstock cost or prevent its delivery altogether. To varying degrees, these scenarios force the use of transmission infrastructure. When the prices of particular feedstocks increase, centralized applications with long-distance transport of hydrogen via truck become more prominent.

This notional study of hydrogen-infrastructure in California highlights several insights regarding the regional build-out of that infrastructure. First, pipeline infrastructure and (to a lesser extent) other transmission infrastructure is non-optimally costly for the levels of demand considered here – it is only when feedstock costs to onsite production technologies are raised substantially (or the deployment of those technologies forbidden) that transmission infrastructure comes into play significantly. Second, some of the potential technologies (e.g., central grid electrolysis) rarely come into use because they are generally more costly than others (e.g. central biomass gasification) in the cost inputs. Third, hydrogen cost may vary widely (an order of magnitude) with locality and with time. Fourth, the construction of production plants that are not fully utilized in the early years of their lifetime substantially increases delivered hydrogen cost in those years.

Conclusions and Future Directions

In summary, HyDS-ME is an effective, integrated, cross-cutting model for optimization-analysis studies of hydrogen infrastructure build-out compatible with the H2A models: it searches for optimal combinations of hydrogen production and transmission infrastructure to meet time-varying demand in urban areas over a region.

The next steps for HyDS-ME are to take the lessons learned in recent applications of the tool and to further exercise its analysis capabilities with ever more realistic input data sets in computing and visualization environments that allow thorough exploration of the cost-issues around regional hydrogen-infrastructure build-out:

- Application of HyDS-ME to more elaborate scenario analyses.
- Directly representing additional key constraints to hydrogen infrastructure build-out explicitly within HyDS-ME:
 - Global constraints on feedstock availability and competition.
 - Right-of-way considerations.

- Accounting for the cost of new or upgraded feedstock-delivery infrastructure.
- More highly localized delivered-feedstock costs.
- Developing a more sophisticated disaggregation of hydrogen demand corresponding to the NAS scenarios.
- Elaborating on the existing HyDS-ME representation of blueprints for infrastructure build-out:
 - Higher resolution of hydrogen infrastructure components.
 - Staged/incremental capacity addition in HyDS-ME, where multiple production facilities (or pipelines) are constructed in a staggered fashion over the years.
 - Fewer conditions on allowable hydrogen infrastructure networks.
 - Directly representing the nuances of hydrogen delivery within urban areas.

FY 2009 Publications/Presentations

1. B. Bush. “Technical Highlights of the Hydrogen Deployment System Modeling Environment (HyDS-ME)”. 27 Aug 2008 & 25 Sep 2008. (presentation)
2. B.W. Bush. “Hydrogen Deployment System Modeling Environment (HyDS-ME): Updates & Enhancements for FY2008”. Strategic Energy Analysis & Applications Center, National Renewable Energy Laboratory, 30 Sep 2008. (report)
3. B. Bush. “Overview of the Hydrogen Deployment System Modeling Environment (HyDS-ME), Version 3.0”. 2 Oct 2008. (presentation)
4. B. Bush, M. Melaina, O. Sozinova, D. Thompson. “Hydrogen Deployment System Modeling Environment (HyDS-ME) Notional California Case Study”. National Renewable Energy Laboratory, 28 Jan 2009. (report)
5. B. Bush, M. Melaina, O. Sozinova, D. Thompson. “HyDS-ME Notional California Case Study”. 5 Feb 2009. (presentation)
6. B. Bush, M. Melaina, O. Sozinova. “Optimal Regional Layout of Least-Cost Hydrogen Infrastructure”. National Hydrogen Association Conference & Expo 2009. (poster)
7. B.W. Bush. “HyDS-ME Interoperability”. Strategic Energy Analysis Center, National Renewable Energy Laboratory, 31 Mar 2009. (report)

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1. Parks, K. *Hydrogen Deployment System Modeling Environment (HyDS ME) documentation milestone report, FY 2006*. NREL/MP-560-40763. Golden, CO: National Renewable Energy Laboratory, October 2006.
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7. National Research Council Committee on Assessment of Resource Needs for Fuel Cell and Hydrogen Technologies. *Transitions to Alternative Transportation Technologies: A Focus on Hydrogen*. Washington, D.C.: National Academies Press, 2008.

VII.8 Analysis of the Hydrogen Production and Delivery Infrastructure as a Complex Adaptive System

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Contract Number: DE-FC36-05GO15034

Subcontractors:

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- Ford Motor Company, Dearborn, MI
- Protium Energy Technologies, Orefield, PA

Start Date: June 15, 2005

Projected End Date: June 30, 2009 (no-cost extension approved through December 31, 2009)

- (A) Future Market Behavior
- (C) Inconsistent Data, Assumptions and Guidelines

Contribution to Achievement of DOE Systems Analysis Milestones

This project will contribute to achievement of the following DOE Systems Analysis milestones from the Systems Analysis section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- **Milestone 5:** Complete analysis and studies of resource/feedstock, production/delivery and existing infrastructure for various hydrogen scenarios. (4Q, 2009)
- **Milestone 25:** Complete the Agent Based Modeling System for infrastructure analysis of hydrogen fuel and vehicles (4Q, 2008)

Accomplishments

- Introduced centralized hydrogen production to the ABM.
- Analyzed the influences on the date of entry of centralized hydrogen production.
- Discovered significant impacts of investor agent's satisficing behavior.
- Introduced into the ABM corporate-level investment decision making in addition to simple project evaluation as the full basis for investment choices.

Objectives

- Use agent-based modeling (ABM) to provide insights into likely infrastructure investment patterns.
- Deal with chicken-or-egg aspect of early transition.
- Provide answer to the question, "Will the private sector invest in hydrogen infrastructure?"

Technical Barriers

This project addresses the following technical barriers from the Systems Analysis section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

Introduction

The purpose of this project work is to analyze investment in hydrogen infrastructure during the early transition to a hydrogen economy using an agent-based modeling and simulation (ABMS) technique. ABMS is a micro-simulation technique that facilitates representation of heterogeneity in terms of many characteristics of the actors (agents) involved in the transition to a hydrogen infrastructure. These characteristics can include size, beliefs and preferences, expectations, goals, and location, among the most important. ABMS simplifies the modeling of learning by agents. In distinction from conventional modeling approaches currently applied to the hydrogen economy, ABMS relies on different objective functions (goals) for

different agents; it also allows for different reactions to unmet expectations, different learning from the emerging economic environment, and different responses based on agent characteristics. It is easy to specify putty-clay capital (an investment in an earlier period of a simulation cannot change into another technology in a subsequent period), which is both realistic and facilitates analysis of quasi-rent changes (stranded investments). Altogether, ABMS is a well-suited vehicle to apply sophisticated economic models in an environment involving actors with widely differing characteristics and goals.

Early transition is expected to be a time of considerable uncertainty, when reasonable investors might hold widely differing expectations and could have different goals. An additional feature of early transition is the existence of a chicken-or-egg problem, in which potential investors in infrastructure want to wait for hydrogen vehicles to emerge on the market, but potential vehicle buyers want to wait until fuel is widely available. ABMS is a convenient tool for exploring these interactions via simulation, since analytical expressions for solutions to models with only modest complications are intractable.

Approach

The project began as a 3-year project with preliminary model results due in the second year, but the project was re-oriented before it began, its first year budget was reduced by nearly 60 percent, and initial funding was delayed. The revised first year goal of the project was to provide an answer to the question, “Will the private sector invest in hydrogen infrastructure?” and to focus on California as a likely region of early transition.

To accomplish the revised first year goal, the project developed a framework that focused on investments as business decisions and used that framework as a basis for preliminary assessment of profitability. In a parallel effort, efforts were begun to prepare the ABM for detailed simulations in the project’s second year. Work in the second year was delayed by a continuing resolution, which restricted staffing. Full funding began in the third year. A revised completion date of June 30, 2009 has been approved. A no-cost extension until December 31, 2009 also has been approved.

Results

Background Review of the Model Structure

The model is composed of two major modules, a driver module which simulates behavior of driver agents, and an investor module which simulates the decisions of the investor agent who supplies hydrogen to

the Los Angeles market. The model uses a geographic information system platform of the Los Angeles metropolitan area based on one-mile grids. Driver agents are located at residential sites corresponding to Los Angeles residential densities. They decide whether to purchase a hydrogen vehicle on the basis of vehicle cost relative to a conventional vehicle, fuel availability, and taste for greenness. Hydrogen production is modeled with investor agents, who make investments in either 1,500 kg/d distributed steam methane reforming stations or centralized production on the basis of their expectations of hydrogen vehicle adoption. They form their expectations from observing past growth in hydrogen vehicles and correct mistakes in expectations from period to period.

Completion of the Model

The prototype model of 2007-08 was completed during 2008-09.

Simulation Results

Results of four important simulations are reported. The first two, the influences of the sticker price of the hydrogen vehicle and of the price of gasoline, are largely market influences, although both can be affected to some extent by policy. The third simulation examines a temporary tax credit policy. The fourth simulation reported here, involving a parameter called the familiarity premium, demonstrates the importance of the preferences of potential hydrogen vehicle purchasers.

Declining Sticker Price

Sensitivity to declining sticker price, shown in Figure 1, shows the effect on sales penetration of moving “too early,” that is, of marketing the hydrogen fuel cell

FIGURE 1. The Effect of Declining Sticker Price on Hydrogen Vehicle Sales Growth

vehicle to a mass audience before technological and scale-economy factors have succeeded in making it cost-competitive with a conventional gasoline vehicle. Jumping the gun by five years has a small (8%) effect on 20-year sales penetration, but if the price remains relatively high for the first 20 years of mass production, it will cause sales to lag more substantially.

Price of Gasoline

In the benchmark scenario, the gasoline price averages \$5.50 per gallon over the period analyzed. Two additional scenarios are tested: one in which the gasoline price averages \$8.00/gallon and the driver agents save 22.8 cents per mile by driving a hydrogen vehicle and one in which gasoline averages \$3.00/gallon and driver agents save only 5.6 cents per mile. The higher savings per mile translates to roughly \$8,000 over the life of the vehicle in expected savings for the average agent, who drives 12,150 miles a year (the benchmark savings for the average agent is about \$4,500). The low savings per mile translates to roughly \$1,400 in expected savings over the life of the vehicle. In Figure 2, the high savings scenario increases hydrogen vehicle market share by roughly one-third, to 90% by the 20th year after introduction. The low savings scenario lowers market share in the 20th year to 32%.

Temporary Tax Credit

Figure 3 shows the consequence of eliminating the vehicle tax credits after ten years. While the drop in the percent of sales once the tax credit is terminated looks drastic, the hydrogen share of vehicle sales continues to climb without a credit, reaching 78 percent of sales after 20 years with the \$3,500 credit and 83 percent with the \$7,000 credit. The temporary tax credit hastens the growth of the hydrogen vehicle stock, which in turn hastens driver agents' familiarity with the vehicle

FIGURE 2. The Effect of Gasoline Price on Hydrogen Vehicle Sales Growth

and bolsters the impact of the bandwagon effect. Without a tax credit, the hydrogen vehicle stock would comprise about 5 percent of the total vehicle stock after 10 years. The tax credits raise the stock at 10 years to 17 percent and 34 percent, which in turn raises the level of the hydrogen share of sales above the no-credit benchmark case for each of the remaining ten years in the simulation.

Familiarity Premium

The familiarity premium is the amount a potential buyer would have to be paid to buy a hydrogen vehicle if he were completely unfamiliar with it. Hydrogen vehicle market share grows more rapidly in the scenario with the lower familiarity premium. In Figure 4, market share reaches 84% by the 20th year, 18% higher than the 20th year market share in the benchmark scenario.

FIGURE 3. Effect of Temporary Tax Credits on Hydrogen Vehicle Sales Penetration

FIGURE 4. The Effect of Familiarity Premium on Hydrogen Vehicle Sales Growth

In the weak bandwagon effect scenario, adoption is substantially slowed, with market share only reaching 49% in the 20th year.

Conclusions and Future Directions

In most of the scenarios studied in this report, hydrogen vehicles ultimately saturate the light-duty vehicle market in Los Angeles. However, these asymptotic market shares generally are reached after the end of the 20-year period reported graphically here. Whether driver agents or investor agents maximize perfectly, or whether they exhibit some behaviors that, strictly speaking, are irrational, has little impact on the ultimate market outcome, although these behaviors can slow down adoption, particularly during the first 10 years of the transition.

In the benchmark scenario, hydrogen vehicles account for 60% of sales within 20 years. However, depending on the values of parameters characterizing driver agent or investor agent attitudes, the 20-year market penetration can range from 35% to 80%. The magnitude of the familiarity premium to driver agents is particularly important to early adoption of hydrogen vehicles. A two-fold variation in the value driver agents place on familiarity with the hydrogen vehicle results in a range of hydrogen vehicle shares of sales from 30% to 80% after 20 years. Alternative degrees of driver preference for greenness, as well as the dispersion of that preference through the population, result in hydrogen vehicle shares of sales ranging from 40% to 70% after 20 years. Nonetheless, none of the driver agent characteristics studied had the capacity to kill the transition. The strength of the bandwagon effect among driver agents has more impact between the 10th and 15th years of the transition than it does by 20 years. Soon thereafter, differences in that behavioral attitude will retain no influence on the transition.

Many of the alternative practices of the investor agents had little impact on the pace of adoption of hydrogen vehicles during the first 20 years. There is little sensitivity to the investor agent's method of estimating demand for hydrogen, and differences in the

sophistication of his expectations formation yields a range of 20-year market penetrations of 45% to 60%. However, while these different investor agent practices do not have major depressing effects on the pace of market penetration, none of the variations studied have the capacity to greatly hasten penetration. This said, one attitude of the investor agent does have the capacity to greatly retard or even kill the transition – very high discount rates on the part of upper management. Discount rates equivalent to very short pay-back periods could keep market penetration to the range of five to 20 percent after 20 years.

External influences can have major impacts on the pace, and even the fate, of the transition. Gasoline prices remaining as low as \$3.00 per gallon for the first 20 years can effectively stall the transition. Conversely, however, a \$5.00 per gallon gasoline price would see the hydrogen vehicle market share rise to 60% in 20 years, and an \$8.00 price would put it at 90%. The price of the hydrogen vehicle relative to the gasoline vehicle has an equally powerful influence. If the hydrogen vehicle remains only \$1,000 higher than the equivalent gasoline vehicle, the hydrogen vehicle share will reach 60% in 20 years, while if it is \$5,000 higher, the share will not exceed 10% after 20 years. On the other side of those possibilities, if the hydrogen vehicle's price were \$3,000 below the gasoline vehicle's price, market penetration would reach 95% in 20 years.

In sum, the answer to the original question, “Will the private sector invest in hydrogen infrastructure?” is, “It depends.” If fuel prices, vehicle production costs, and a number of driver and investor parameters are favorable, the private sector will invest in the infrastructure necessary to support the transition to hydrogen.

FY 2009 Publications/Presentations

1. Mahalik, M., C. Stephan, G. Conzelmann, M. Mintz, G. Tolley, and D. Jones, “Modeling Investment Strategies in the Transition to a Hydrogen Transportation Economy,” *Proceedings of the NHA Conference and Hydrogen Expo*, Columbia, SC, March 30 – April 3, 2009.

VII.9 Adapting the H2A Hydrogen Production Cost Analysis Model to Stationary Applications

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Project Start Date: January 1, 2008
Project End Date: September 30, 2009

Objectives

- Expand the H2A Power Model's capabilities to enhance modeling and evaluation of stationary combined production of electricity, heat, and hydrogen.
- Use case studies to demonstrate the enhanced H2A Power Model's functionality and value for modeling systems in various geographic locations and building types.

Technical Barriers

This project addresses the following technical barriers from the Systems Analysis, Technical Challenges section (4.5) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (B) Stove-piped/Siloed Analytical Capability
- (C) Inconsistent Data, Assumptions and Guidelines
- (D) Suite of Models and Tools
- (E) Unplanned Studies and Analysis

Contribution to Achievement of DOE Systems Analysis Milestones

This project is contributing to achievement of the following DOE milestones from the Systems Analysis section of the Hydrogen, Fuel Cells and Infrastructure

Technologies Program Multi-Year Research, Development and Demonstration Plan:

- **Milestone 5:** Complete analysis and studies of resource/feedstock, production/delivery and existing infrastructure for various hydrogen scenarios. (4Q, 2009)
- **Milestone 26:** Annual model update and validation. (4Q, 2009)
- **Milestone 39:** Annual update of analysis portfolio. (4Q, 2009)

Accomplishments

- Completed all modifications and additional functionality identified in the scope of work.
- Published Version 1.1 of the H2A Power Model.
- Used case studies to demonstrate the enhanced functionality of Version 1.1 and its value for modeling systems in various geographic locations and building types.

Introduction

The U.S. Department of Energy's H2A platform is a Microsoft Excel-based economic analysis model that provides transparent, consistent, and comparable results for DOE's hydrogen modeling efforts. H2A hydrogen production and delivery models geared toward use of hydrogen as a vehicle fuel have been in use for several years. However, stationary fuel cell systems that produce electricity, heat, and hydrogen – known as “tri-generation” systems – also offer potential advantages: lower hydrogen production cost, inherently distributed hydrogen production, lower fossil energy use and greenhouse gas emissions, reduced electricity transmission congestion, lower capital investment risk, and backup power functionality. DOE views tri-generation systems as critical for early fuel cell market transformation and requires modeling to evaluate the potential costs and benefits. As a result, the H2A platform was adapted to create the H2A Power Model.

The H2A Power Model analyzes the technical and economic aspects of high-temperature fuel cell-based tri-generation systems. This type of system would provide onsite-generated heat and electricity to large end users such as hospitals and office complexes. The hydrogen produced could be used for fueling vehicles or stored for later conversion to electricity. In the

model, users select which technologies are used in the system – such as hydrogen fuel cells, photovoltaic panels, and electrolyzers – and define each technology's cost and performance parameters (Figure 1). Users also select fuel costs and demand priority (i.e., whether the system follows electricity or heat demand) and can accept default H2A financial parameters or enter custom parameters. Hourly electricity, heat, and hydrogen demand profiles and renewable energy supply profiles can be entered or selected from databases. The model uses the inputs, default values and calculations, and a standard discounted cash flow rate of return methodology to determine the cost of delivered energy, with reference to a specified after-tax internal rate of return. It also determines the amount and type of energy input and output and the associated greenhouse gas emissions. Version 1.0 of the H2A Power Model was completed in Fiscal Year 2008. A second fuel cell system (molten carbonate) was added in Version 1.1. Version 1.1 also expands the input options and enhances energy and cost output information for tri-generation systems.

Approach

The potential advantages of a fuel cell–based tri-generation system depend on numerous variables, including the type of building using the system, geographic location, utility grid interaction, financial assumptions, and economic incentives. To evaluate the cost of producing electricity, heat, and hydrogen accurately, the H2A Power Model analyzes energy supply and demand for each hour over the course of a year. The enhancements to Version 1.1 enable the model to perform this hourly analysis more accurately and with more flexibility with regard to fuel cell and renewable electricity technologies used, building energy demand, costs, and revenues. Case studies evaluated

using Version 1.1 demonstrate the model's functionality and value for modeling systems in various geographic locations and building types.

Results

The following enhancements were added to Version 1.1 of the H2A Power Model:

- Standard building load profile import capability
- Solar and wind resource data import capability
- Individual depreciation for all components
- Economic incentives analysis
- Detailed grid power purchase structure
- Net metering functionality
- Greenhouse gas tables from GREET 1.8b
- Financial summary sheet
- Sensitivity analysis/tornado charts
- Choice of phosphoric acid or molten carbonate fuel cell system

In addition, a user guide was produced and training was provided for an initial group of users. Feedback from a first round of peer review was incorporated into the model. A second round of peer review is ongoing.

Version 1.1 was used to analyze the influence of building type and geographic location on the economics of tri-generation systems. Electricity and heat demand profiles from the National Renewable Energy Laboratory's building systems model were entered for high schools, hospitals, large office buildings, large hotels, and supermarkets in six U.S. cities representing six climate zones. The buildings' electricity demand included air conditioning, and heat demand included space and hot water heating.

These analyses provided insight into the optimal size of the fuel cell system as a function of building type and location; Figure 2 shows an example analysis. Climate was shown to influence the cost of energy because of its effect on fuel cell utilization; Table 1 and Figure 3 show an example analysis. The impacts of electricity and natural gas prices on the cost of hydrogen were also shown: when electricity prices are high, electricity produced by the fuel cell can be "priced" higher, thus reducing the cost of hydrogen; when natural gas prices are low, the fuel cell tri-generation system produces electricity, heat, and hydrogen for a lower cost.

Conclusions and Future Directions

Version 1.1 of the H2A Power Model was developed. Improvements over the previous version enable more accurate and flexible analysis of hourly energy supply and demand and the resulting cost of

FIGURE 1. H2A Power Model tri-generation system component selection diagram. The user need not use all energy conversion technologies; for example, a standalone fuel cell system can be evaluated.

FIGURE 2. H2A Power Model results showing the cost of energy from a tri-generation system as a function of fuel cell maximum electricity output for hospitals in different cities/climate zones.

TABLE 1. H2A Power Model comparison of fuel cell size, hydrogen delivered, and fuel cell utilization for hospitals in different cities/climate zones showing higher fuel cell utilization in warmer climates.)

	Fuel Cell Size (kW)	Hydrogen Delivered (kg/day)	Fuel Cell Utilization (AC Output/Max AC Output)
MIAMI	846	328	81.2%
HOUSTON	799	296	78.0%
LOS ANGELES	640	236	77.4%
HELENA	629	225	75.3%
BALTIMORE	684	244	75.2%
CHICAGO	646	230	74.9%

FIGURE 3. H2A Power Model results showing lower hydrogen cost for cities in warmer climates with higher fuel cell utilization.

hydrogen, heat, and electricity. Version 1.1 was used to analyze the influence of building type and geographic location on the economics of tri-generation systems. This information can be used to evaluate where and for what building applications tri-generation systems would be most economic.

Future work includes continuing to improve the functionality of the H2A Power Model: results from an extensive second round of peer reviews will be incorporated into the model, and the ability to model absorption chillers will be added. Model training and documentation will be made available, and ongoing support and maintenance will be performed.

The H2A Power Model will continue to support DOE analysis of hydrogen infrastructure implementation scenarios and market transformation strategies. The model also will be integrated with DOE's Macro Systems Model.

FY 2009 Publications/Presentations

1. H2A Power Model Presentation, presented at the Transportation and Stationary Power Integration Workshop, Phoenix, Arizona, November 27, 2008.
2. H2A Power Model Presentation, presented at the CHBC General Meeting, Diamond Bar, California, December 11, 2008.
3. H2A Power Model Presentation, presented at the Association of Energy Engineers Southern California Chapter Meeting, March 12, 2009.
4. The Influence of Building Location on Combined Heat and Power/Hydrogen (Tri-Generation) System Cost, Hydrogen Output and Efficiency, presented at the National Hydrogen Association Meeting, Columbia, South Carolina, March 30 – April 3, 2009.
5. H2A Power Model Presentation, presented at the National Hydrogen Association Meeting, Columbia, South Carolina, March 30 – April 3, 2009.
6. Adapting the H2A Hydrogen Production Cost Analysis Model to Stationary Applications, presentation at the DOE Hydrogen Program Annual Merit Review and Peer Evaluation, Washington, D.C., May 19, 2009.
7. H2A Power Model Startup Guide, April 2009.

VII.10 Hydrogen and Fuel Cell Analysis: Lessons Learned from Stationary Power Generation

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Contract Number: DE-FG36-07GO17107

Project Start Date: October 1, 2007
Project End Date: September 30, 2009

Objectives

Three main project objectives include:

- quantifying and critical analyzing lessons learned from stationary power programs,
- demonstrating best practices, and
- recommending research, development and demonstration (RD&D) strategy related to stationary fuel cells.

Sub-objectives include:

- consideration of environmental and safety concerns,
- education of key stakeholders, and
- delineating early market applications and transformation.

Technical Barriers

This project primarily addresses the following technical barriers from the Systems Analysis section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

(A) Future Market Behavior

Contribution to Achievement of DOE Systems Analysis Milestones

This project will contribute to achievement of the following DOE milestones from various sections of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

3.2.6 Task 1: Delivery Infrastructure Analysis

- Milestone 2: Identify cost-effective options for hydrogen delivery infrastructure to support the introduction and long-term use of hydrogen for transportation and stationary power. (4Q, 2007)

4.7 Task 1: Perform Studies and Analysis

- Milestone 4: Complete a “lessons learned” study of the development of other infrastructures which apply to hydrogen fuel and vehicles. (4Q, 2008)

3.4.6 Task 8: Stationary and Other Early Market Fuel Cells

- Milestone 67: Determine whether to continue stationary fuel cell system R&D based on progress towards meeting targets. (4Q, 2011)

3.7.4 Task 4: Domestic Standards

- Milestone 21: Completion of necessary codes and standards needed for the early commercialization and market entry of hydrogen energy technologies. (4Q, 2012)

Accomplishments

- Compilation and data collection related to projects and programs.
- Distribution of online survey and hosting of Stationary & Portable Fuel Cell Market Transformation and Applications Workshop.
- Analysis of lessons learned, draft best practices and strategy recommendations.

Introduction

This study is considering opportunities for hydrogen in stationary applications in order to make recommendations related to RD&D strategies that incorporate lessons learned and best practices from relevant national and international stationary power efforts. The study will identify the different challenges and opportunities for producing and using hydrogen as an energy carrier. By identifying the lessons learned from prior stationary power programs, including the most significant obstacles, how these obstacles have been approached, outcomes of the programs, and how this information can be used by the Hydrogen, Fuel Cells & Infrastructure Technologies Program to overcome barriers and achieve milestones related to the implementation of fuel cell technologies for distributed stationary power.

Approach

The approach consists of compilation and classification of programs, establishment of contacts, program data collection, including questionnaires, workshops, and site visits. Finally, lessons learned and best practices are being analyzed to develop strategy recommendations. The information collected is currently being incorporated into the analysis leading toward lessons learned and best practices for stationary fuel cell research and development, as well as early market penetration and market transformation. The lessons learned from the programs are being used in order to establish best practices and provide recommendations for a hydrogen strategy that addresses opportunities for hydrogen in stationary power generation systems. As required, this strategy will analyze all hydrogen pathways and a combination of distributed power generating stations, and provide an overview of stationary power markets, benefits of hydrogen-based stationary power systems, and competitive and technological challenges.

Results

To date, nearly 100 respondents have participated in the survey. By acquiring the fuel cell customer/end-user opinion on the current status of the stationary fuel cell market, we have gained knowledge pertaining to what steps need to be taken to make recommendation on how to bring more customers into the fuel cell market.

One of the initial questions asked was to provide information on how many years had elapsed between initial planning and implementation of their fuel cell project. It is important to evaluate this duration of time as to better understand how much time was spent for risk analysis, budget management, cost-benefit analysis, and verifying that their site met applicable

codes and standards. Of the respondents who were able to answer the question with confidence, 59.4% of the respondents stated the time between initial planning and implementation was 2 years or less. This shows quick action was taken to get a large majority of the projects operational and that few obstacles stood between initial planning and actual implementation. Also, 69.0% of the projects became operational between the years of 2005 and 2008, which shows there has been a large push for fuel cell implementation in recent years. This push is most likely due to factors including support for alternative energy solutions, rising energy costs, and environmental reasons. The duration of time in which the fuel cell was in operation is also a critical statistic for this study since initial planning incorporates a significant portion of initial costs.

Figure 1 shows the largest percentage of the respondent's fuel cells are still in operation, which indicates a correlation to a trend of increasing life expectancy of fuel cells. Although the 24.14% of projects with less than one year of operation seems to point to the contrary of the earlier statement, further analysis of the data shows that most of these projects had less than a one year lifespan because the purpose of those projects was for proof of concept and demonstration. Since proof of concepts and demonstrations rarely last longer than one year, it is apparent why 24.14% of the respondents had a project whose lifespan of less than one year.

Another important category of questions asked the respondents to discuss the types of application implemented in their program, which type of fuel cell was installed, and what type of fuel was used in the program. Not surprisingly, the vast majority of fuel cell projects were fueled by hydrogen and natural gas, 51.5% and 24.2%, respectively, with other fuel sources being JP-8 (kerosene-based jet fuel), LPG (liquefied petroleum gas), and methanol. This supports the opinions of many fuel cell advocates, which suggest hydrogen could be the future for both stationary and transportation alternative energy power applications.

FIGURE 1. Responses to Question 5, "If the fuel cell is no longer operational, how many years did it operate?"

The popular types of applications used by the pool of respondents were backup power, material handling equipment, and grid independent power. From the data shown in Figure 2, backup power shows to be the typical application used in the respondents' programs.

Intriguingly, of those types of applications shown in Figure 2, 37.0% were grid connected systems, which encourages optimism for future fuel cell projects that wish to take advantage of grid connected systems and the opportunities they provide for backup power and reliability.

As shown in Figure 3, the range of answers was wide when the respondents were asked to describe the cost-effectiveness of the program in terms of investment vs. market success/failure. Successful programs highlighted the fact that their fuel cells operated excellently without constant maintenance, high initial costs were subsidized (by the government), ability to promote "green" behavior, and the repeatability of demonstrations. Whereas reasons for unsuccessful programs included success in proving technology but total investment did not lead to proving the cost effectiveness of the fuel cell

FIGURE 2. Responses to Question 7, "What type of application was implemented in your program?"

FIGURE 3. Responses to Question 21, "How would you describe the cost-effectiveness of the program (investment vs. market success/failure)?"

solution, high initial investment, and varying regional energy prices. Programs which were in need of constant power for primary power applications discovered problems pertaining to constant fuel cell durability along with significant delays in acquiring spare parts for failed components.

In addition, feedback gathered through site visits and a workshop are being incorporated into the results. A wide variety of lessons learned, best practices, and suggestions for early market development strategies, as well as opinions on what actions should be taken regarding policies for promotion of technical RD&D were compiled.

Conclusions and Future Directions

Research continues on the *preliminary conclusions*:

- The role and use of hydrogen fuel cells in stationary applications can be significant in portable applications, niche markets, distributed generation or co-generation.
- Market penetration is the ultimate goal of the energy related industries, but early markets must be strategically aligned with balancing near-term and long-term objectives.
- Focus on demonstrating that cost, durability, and reliability can be met for early markets (with incentives, if necessary).
- Consider opportunities and trade-offs for stationary applications in conjunction with the other application sectors, e.g., providing fuel for transportation applications.
- Take a systems perspective – components should address multiple systems.

A related response was also provided for Request for Information DE-PS36-09GO3900.

Special Recognitions & Awards/Patents Issued

1. "Stationary & Portable Fuel Cell Market Transformation and Applications Workshop", Held at *National Hydrogen Association Annual Conference and Expo*, Columbia, April 2, 2009.

FY 2009 Publications/Presentations

1. Cottrell, C.A., Thomas, M., and Grasman, S.E., "Best Practices for Stationary and Portable Fuel Cell Markets", *World Congress of Young Scientists on Hydrogen Energy Systems*, Turin, October 2009.
2. Cottrell, C.A., and Grasman, S.E., "A Preliminary Study on Lessons Learned from Stationary and Portable Fuel Cell Applications", *Proceedings of the IIE Research Conference and Exhibition*, Miami, May 2009.

3. Grasman, S.E., “Hydrogen and Fuel Cell Analysis: Lessons Learned from Stationary Power Generation”, *US Fuel Cell Council Member Meeting*, March 2009.
4. Grasman, S.E., “Hydrogen and Fuel Cell Analysis: Lessons Learned from Stationary Power Generation”, *US Fuel Cell Council Webinar*, November 2008.
5. Grasman, S.E., “Transitional Hydrogen Supply Chain Modeling”, *INFORMS National Meeting*, Washington, DC, October 2008 [invited].

VII.11 Development of HyTrans Model and Integrated Scenario Analysis

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Project Start Date: October 1, 2005
Project End Date: September 30, 2010

Objectives

The HyTrans model is a dynamic, non-linear market simulation model in which all the key components of a transition to hydrogen vehicles are represented: hydrogen supply, vehicle manufacturing and consumer purchase and use. Its objectives are to:

- Simulate market behavior in the transition to hydrogen-powered vehicles.
- Analyze the impacts of technological goals on the transition.
- Measure the economic costs and benefits.
- Estimate the impacts on greenhouse gas emissions and oil dependence.
- Create and analyze credible scenarios of the transition to hydrogen vehicles.
- Evaluate the impacts of alternative policies on the transition to hydrogen.

Technical Barriers

This project addresses the following technical barriers from the Systems Analysis, Technical Barriers section (4.5) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) Future Market Behavior: especially the interdependencies and linkages of hydrogen supply,

vehicle supply and the demand for vehicles and hydrogen.

- (B) Stove-piped/Siloed Analytical Capability: coordinating and integrating analysis resources across all facets of the analytical domain.
- (D) Suite of Models and Tools: improving HyTrans as a component model of the suite to make it more usable and consistent.
- (E) Unplanned Studies and Analysis: such as analysis of potential delays in meeting technical program objectives and potential impacts of falling short of initial on-board hydrogen storage goals.

Contribution to Achievement of DOE Systems Analysis Milestones

This project will contribute to achievement of the following DOE milestones from the Systems Analysis section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- **Milestone 5:** Complete analysis and studies of resource/feedstock, production/delivery and existing infrastructure for various hydrogen scenarios. (4Q, 2009)
- **Milestone 8:** Complete analysis and studies of resource/feedstock, production/delivery and existing infrastructure for technology readiness. (4Q, 2014)
- **Milestone 26:** Annual model update and validation. (4Q, annually)

Accomplishments

- Completed updating of the HyTrans model and calibration to the 2009 Annual Energy Outlook projections, including High and Low Oil Price Scenarios.
- Completed revision of HyTrans' representation of fuel cycle greenhouse gas emissions to accurately represent the latest version of the Greenhouse gases, Regulated Emissions and Energy use in Transportation (GREET) model, and to incorporate emissions representations for new vehicle technology characterizations.
- Completed updated characterization of advanced vehicle technologies, including plug-in hybrid vehicles (PHEVs) based on multiple sources: Argonne National Laboratory (ANL) Powertrain Systems Analysis Toolkit (PSAT) runs, Multipath Study Scenarios, Massachusetts Institute of Technology (MIT) and European Union (EU) Conservation of Clean Air and Water in Europe

(CONCAWE) scenarios. Integrated new technology representations into HyTrans, adding PHEVs for both conventional internal combustion engine (ICE) and fuel cell vehicles (FCVs) as technology options.

- In collaboration with ANL PSAT modelers, developed a new method for determining the optimal range and therefore optimal storage capacity of hydrogen-powered vehicles, for use in assessing the impacts of storage technology on hydrogen vehicle market success.
- Updated HyTrans to include the latest version of the Hydrogen Delivery Scenario Analysis Model (HDSAM) model (Version 2.0 downloaded 12/10/2008), adding a new representation of delivery options that distinguish between urban and rural environments, and include additional modal choices, such as cryo-compressed trucks. Delivery is now separately determined for transmission and local distribution allowing a greater diversity of solutions.
- Updated HyTrans to include the latest version of the updated versions of the H2A Production model (H2A Production Case Studies, downloaded 12/10/2008).
- Published Edition 28 of the Transportation Energy Data Book: posted on its Web site on June 29, 2009, available in hardcopy on July 13, 2009.
- Analysis of the impacts of alternative technical achievements for on-board hydrogen storage on the potential market for hydrogen vehicles (to be completed in Fiscal Year 2009).
- Analysis of the effects of delays in achieving DOE Hydrogen FCV Program goals on market success and reductions in U.S. oil dependence and greenhouse gas (GHG) emissions (to be completed in FY 2009).

Introduction

The HyTrans model simulates a market transition of U.S. light-duty vehicles from conventional petroleum-powered internal combustion engines to hydrogen, from the present until 2050. The purposes of the HyTrans model are to assess the impacts of achieving research and development goals on the market success of hydrogen vehicles and hydrogen as an energy carrier, to develop credible visions of the transition to hydrogen-powered transportation, to estimate the potential benefits and costs of the transition, and eventually to understand the role of policy as well as technology in achieving the transition. The market success of hydrogen and hydrogen-powered vehicles, including the decisions of energy suppliers to produce and deliver hydrogen, the decisions of manufacturers

to build and sell hydrogen-powered vehicles and the decisions of consumers to buy and use the vehicles, are all determined within the HyTrans model. An important contribution of HyTrans is the explicit representation of technological progress and cost reductions over time. These features make HyTrans unique among existing models of the evolution of hydrogen-powered transportation.

The modeling capabilities acquired in developing the HyTrans model were applied to analyzing the potential to create a sustainable domestic proton exchange membrane (PEM) fuel cell industry by means of a government acquisition program for non-automotive PEM fuel cells. Relying on existing market research and in-depth interviews with original equipment manufacturers a simulation model was developed to estimate the impacts of government PEM fuel cell purchases on learning-by-doing and scale economies in the non-automotive PEM fuel cell industry. Building on this research, analysis of stationary fuel cell applications will be significantly expanded in FY 2010.

Approach

Hydrogen and FCVs will compete with other alternative energy sources and advanced automotive technologies in the marketplace. Our approach is to combine representations of the best available models of hydrogen production, delivery, manufacturing, and consumer demand into an integrated representation of the U.S. market for vehicles and fuels. This model can be calibrated to national or international energy market scenarios, such as the Energy Information Administration's Annual Energy Outlook. Using competitive economic theory, the HyTrans model then calculates how advanced technologies and supporting policies could change the future evolution of vehicles and their energy use. The key feature of the integrated market modeling method is that the decisions of the participants in the market, hydrogen suppliers, vehicle manufacturers and consumers, are fully interdependent. That is, the model simulates the market solution to the "chicken or egg" problem faced by alternative energy systems by explicitly representing the roles of barriers such as learning-by-doing, economies of scale, limited fuel availability and limited make and model choice.

HyTrans is a tool for integrated analysis; it depends on other models and assessments for key inputs. HyTrans relies on the H2A production models to represent the cost of hydrogen supply, the H2A delivery model to estimate the costs of delivery and retailing, the GREET model for the energy and emissions of alternative production and use pathways and the PSAT model for vehicle technology characterizations. This year, in addition to updating and expanding its capabilities, HyTrans has been used in two analyses:

1. Assessment of the impacts of delays in achieving technical targets on the timing and ultimate success of hydrogen vehicles and their ability to reduce oil dependence and GHG emissions.
2. Assessment of the impacts of alternative hydrogen storage technologies and pathways on the transition to hydrogen FCVs.

Results

The major focus of FY 2009 has been updating and enhancing the HyTrans model to reflect significant improvements in related models, new oil price scenarios, and a more complete and up-to-date representation of advanced vehicle technologies. Most of the major submodels received a complete updating:

- HyTrans production submodel was updated to represent in reduced form the revised H2A model (downloaded 12/10/2008).
- HyTrans delivery model was restructured and updated to reflect HDSAM Version 2.0 (downloaded 12/10/2008).
- HyTrans scenarios to 2050 were recalibrated to conform to the 2009 Annual Energy Outlook Reference, Low Oil Price and High Oil Price Projections.
- Updated HyTrans to reflect latest version of GREET model and enhance representation of fuel cycle GHG emissions. Lifecycle emissions estimates for nine hydrogen production pathways were updated using GREET_1.8b.xls. Wind energy was added as one of the hydrogen production pathways.
- Modified HyTrans' vehicle technology choice structure to include PHEV versions of conventional ICE vehicles and PHEV versions of hydrogen FCVs. Analysis of the impacts of this change will be completed in FY 2009.
- Conducted an analysis of the impacts of a ten-year delay in achieving DOE program goals for hydrogen FCV technology on the timing and degree of market success of FCVs and their impacts on U.S. oil dependence and GHG emissions. The results will be documented in a memorandum to be completed in FY 2009.
- Conducted an analysis of the potential effects of alternative on-board hydrogen storage goals on the timing and degree of market success of FCVs. Four alternative energy densities and storage costs were considered. The results will be documented in a memorandum to be completed in FY 2009.
- Published Edition 28 of the Transportation Energy Data Book: posted on its Web site on June 29, 2009, available in hardcopy on July 13, 2009. Copies have been distributed to over 1,000 researchers in 31 countries.
- Updated the ORNL Oil Security Metrics Model and calibrated it to the Annual Energy Outlook 2009 Reference, Low Oil Price and High Oil Price Projections. The model was used to estimate the impacts of DOE's Vehicle Technologies Program on U.S. Oil Dependence through 2050. A paper making use of the Oil Security Metrics Model, proposing a measurable definition of oil independence and assessing what would be required to achieve it was peer-reviewed and published in the journal *Energy Policy*.
- Developed a methodology, in collaboration with ANL, for defining the optimal on-board storage for hydrogen vehicles as a function of vehicle technical performance and storage cost. The method trades off the marginal value of range to car owners versus its marginal cost, as a function of fuel availability, of achieving that range in a hydrogen FCV (Figure 1). The pattern of results is intuitive: as the cost of on-board storage increases, less on-board storage is preferred; as fuel availability increases, less on-board storage is optimal. This suggests that the earliest FCVs should be designed with greater amounts of on-board storage than will be required in later years when hydrogen fuel is more widely available. Though not surprising, these results represent the first quantification of these relationships for advanced technology, alternative fuel vehicles.

FIGURE 1. Optimizing Fuel Cell Vehicle Range

- Vehicle technology characterizations were updated based on PSAT and MultiPath Study data. Four major sources of advanced vehicle cost projections were identified and detailed results (including assumptions) were summarized. Two of the sources were based on the latest DOE studies using the PSAT model. Based on this analysis, two alternative cost scenarios have been developed and will be documented in a technical memorandum in FY 2009. The cost scenario reflecting full accomplishment of DOE's program goals is illustrated for passenger cars in Figure 2. A key performance attribute, fuel economy, is likewise shown for the two scenarios in Figures 3 and 4.

Conclusions and Future Directions

The comprehensive updating and enhancement of the HyTrans model accomplished in FY 2009 positioned the model for new analyses of a variety of significant questions. Analysis of the potential impacts

of alternative on-board storage technology was initiated prior to the writing of this report and will be completed by the end of FY 2009. Likewise, model runs analyzing the effects of delays in reaching program goals on the impacts of hydrogen vehicles has been completed and will be documented in a memorandum this fiscal year. Finally, an analysis of the effects of PHEV technology on the success of FCVs will be initiated in FY 2009 with the intent of completing it during the fiscal year. Innovations developed during the creation of a PHEV model for Vehicle Technologies will be incorporated in HyTrans, as well.

The experience gained in building an integrated market model integrating supply of hydrogen, supply of vehicles, and demand for and use of vehicles will be useful in the coming fiscal year in transitioning to a greater emphasis on stationary fuel cell deployment and its role in the transition to hydrogen. The HyTrans team members will be joined by a new post-doctoral staff member with experience in modeling and optimization applied to automotive technology policy analysis.

FIGURE 2. Long-Run Retail Prices of Advanced Technology Passenger Cars: Program Goals Met

FIGURE 3. Fuel Economies of Advanced Technology Passenger Cars: Program Goals Met

FIGURE 4. Fuel Economies of Advanced Technology Passenger Cars: Alternative Case

Special Recognitions & Awards/Patents Issued

1. Dr. David L. Greene was selected to the Energy Efficiency Hall of Fame by the Alliance to Save Energy in FY 2009.
2. Dr. David L. Greene received the Science Communicator of the Year Award from UT-Battelle in November, 2008.

FY 2009 Publications/Presentations

1. Greene, D.L., "Measuring Energy Security: Can the US Achieve Oil Independence?", published online, *Energy Policy*, May 2009.
2. Leiby, P.N, D.L. Greene, Z. Lin, D. Bowman, S. Das, "Modeling the Transition to Advanced Vehicles and Fuels", a presentation to the MIT-Ford-Shell Workshop: "Strategies for Market Transitions to Alternative Energy Transportation Systems", June 9, 2008.
3. Davis, S.C., S.W. Diegel, R.G. Boundy, *Transportation Energy Data Book: Edition 28*, ORNL-6984, June 2009.

VII.12 Fuel-Cycle Analysis of Hydrogen-Powered Fuel Cell Systems with the GREET Model

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Project Start Date: October 2002
Project End Date: Project continuation and
direction determined annually by DOE

Objectives

- Expand and update the Greenhouse gases, Regulated Emissions, and Energy use in Transportation (GREET) model for hydrogen production and delivery pathways and for applications involving fuel cell vehicles (FCVs) and other early market fuel cell (FC) systems.
- Examine well-to-wheels (WTW) energy and greenhouse gas (GHG) emission effects of plug-in hybrid electric vehicles (PHEVs).
- Conduct fuel-cycle analysis of early market FC systems for combined heat, hydrogen, and power (CHHP) as well as combined heat and power (CHP) applications.
- Provide WTW results for DOE Office of Hydrogen, Fuel Cells, and Infrastructure Technologies activities such as the Hydrogen Posture Plan and the Multi-Year Program Plan.
- Engage in discussions and dissemination of information on the energy and environmental benefits of hydrogen FCVs and other FC systems.

Technical Barriers

This project addresses the following technical barriers from the Systems Analysis section of the Hydrogen, Fuel Cells, and Infrastructure Technologies Program Multi-Year Research, Development, and Demonstration Plan:

- (C) Inconsistent Data, Assumptions, and Guidelines
- (D) Suite of Models and Tools
- (E) Unplanned Studies and Analyses

Contribution to Achievement of DOE Systems Analysis Milestones

This project contributes to achievement of the following DOE milestone from the Systems Analysis section of the Hydrogen, Fuel Cells, and Infrastructure Technologies Program Multi-Year Research, Development, and Demonstration Plan:

- **Milestone 11:** Complete environmental analysis of the technology environmental impacts for the hydrogen scenarios and technology readiness.

Accomplishments

- Completed the analysis of energy use and GHG emissions of polymer electrolyte membrane (PEM) FC application to forklifts, which showed that significant reductions in energy use and GHG emissions can be accomplished by displacing fossil fuels in internal combustion engine (ICE) forklifts and replacing battery-powered forklifts with those powered by FCs using hydrogen from steam reforming of natural gas or from coke oven gas.
- Completed the analysis of energy use and GHG emissions associated with various FC technologies for distributed power generation, which showed that FC technologies approaching or exceeding the DOE target electrical efficiency of 40% offered a significant reduction in energy use and GHG emissions compared to combustion generation technologies and U.S. grid generation mix.
- Conducted a WTW analysis of PHEVs, including FC PHEVs, which showed that PHEVs offered significant reduction in petroleum energy use and GHG emissions relative to a conventional ICE vehicle that used gasoline.
- Conducted energy and GHG effects of FC systems for CHHP generation, which showed that CHHP FCs offer significant reduction in energy use and GHG emissions compared to CHP FCs and distributed combustion generation technologies.

Introduction

The pathway to the application of PEM FCs in hydrogen vehicles will likely be preceded by the introduction of PEM FCs in markets with fewer technical challenges than automobiles. Forklifts and distributed power generation are near-term markets in which PEM FC can be successful. The application of FCs to distributed power generation has the potential to produce excess hydrogen at a relatively low cost for local utilization. The excess hydrogen may be stored locally and used to refuel FC forklifts in a nearby facility or to refuel hydrogen FCVs during their early introduction in the marketplace. Recently, PHEVs received significant attention for their potential of reducing the dependence of the U.S. transportation sector on petroleum by using off-peak excess electric generation capacity and increasing the energy efficiency of vehicles. While PHEVs offer the potential for reductions in petroleum energy use and GHG emissions, these potential benefits need to be thoroughly examined by including the upstream energy and emissions penalties associated with the electricity generation needed to recharge PHEV batteries. The implications of the upstream marginal electricity generation mix as well as the PHEV's powertrain technology, fuel source, and all-electric range (AER) rating can be fully understood through a WTW assessment of energy use and GHG emissions.

The GREET model has been expanded to address the fuel-cycle energy use and GHG emissions associated with the application of CHP and CHHP FCs and to examine the WTW energy use and GHG emissions of PHEVs. In March 2009, Argonne released version 1.8c of the GREET model. As of the latest release, more than 10,000 researchers worldwide have become registered GREET users.

Approach

GREET obtains data needed for simulating different fuel cycles and WTW pathways from the open literature, simulation results from Hydrogen Analysis (H2A) production and delivery models, the H2A Power model, and process engineering simulation models such as Advanced System for Process Engineering (ASPEN). GREET uses simulation results from the Powertrain System Analysis Toolkit (PSAT) model to estimate fuel economy for hydrogen FCVs, PHEVs, and other advanced fuel/vehicle technologies. GREET researchers also interact with industry sources and users to obtain data on the performance characteristics of systems and components associated with the simulated pathways. Then, the GREET model was expanded and updated to conduct WTW and fuel-cycle simulations for the pathways of interest. GREET examines fuel-cycle energy use and emissions for baseline and alternative technologies by tracking the energy use and emission

occurrences throughout the upstream processes to the primary source of energy for each technology. The fuel cycle includes the production and transportation of the primary energy source or feedstock (e.g., crude oil or natural gas [NG]) to the fuel production plant, the conversion of the primary energy source in the production plant to a fuel suitable for each technology (e.g., NG to hydrogen [H_2] or NG to electricity), the conditioning of the fuels (e.g., H_2 compression, direct current-to-alternating current electricity inversion, etc.), and the end use of the conditioned fuels (e.g., H_2 in forklifts or NG in distributed power generators).

Results

The fuel-cycle results for various distributed generation technologies were examined based on estimates of annual production and consumption of energy streams as produced by National Renewable Energy Laboratory's H2A Power Model for different facility types in different climatic regions. Two different approaches for fuel-cycle analysis were considered: a total demand approach and a displacement approach. The total demand approach compared the impact of various technologies in satisfying a facility's demand for electric and heat energy, which includes the onsite generation of power, heat, and hydrogen in addition to typical technologies for producing supplemental heat, hydrogen, and the grid power. The displacement approach examined different technologies for onsite generation of electricity and evaluated credits for the co-products of heat and hydrogen. Figures 1 and 2 show the fuel-cycle GHG emissions associated with different generation technologies for a hospital in Chicago using the total demand approach and the displacement approach, respectively. The relative benefits of the CHP and CHHP systems depend on the efficiency and carbon intensity of the displaced grid mix. In general, CHHP FCs are shown to provide more reduction in energy use

FIGURE 1. Fuel Cycle GHG Emissions for a Hospital in Chicago Using the Total Demand Approach

FIGURE 2. Fuel Cycle GHG Emissions for a Hospital in Chicago Using the Displacement Approach

and GHG emissions compared to CHP FC systems. Utilization of co-produced heat is critical to the overall energy and emission performance of FC systems. CHHP FCs provide better utilization of the coproduced heat compared to CHP FC systems.

Three North American Electric Reliability Corporation regions (4, 6, and 13) were selected for the WTW analysis of PHEVs, because they encompassed large metropolitan areas (Illinois, New York, and California, respectively) and provided significantly different marginal generation mixes for recharging PHEVs. The electricity generation for PHEV recharging also included the U.S. generation mix and electricity from renewable sources in examining cases of average and clean mixes, respectively. For an AER between 10 mi and 40 mi, PHEVs that employed petroleum fuels (gasoline and diesel), a blend of 85% ethanol and 15% gasoline (E85), and hydrogen offered a 40–60%, 70–90%, and more than 90% reduction in petroleum energy use and a 30–60%, 40–80%, and 10–100% reduction in GHG emissions, respectively, relative to an ICE vehicle that used gasoline, as shown in Figure 3. The spread of WTW GHG emissions among the different fuel production technologies and grid generation mixes was wider than the spread of petroleum energy use due to very different carbon intensities of the diverse fuel production technologies and feedstock sources for the fuels considered in this analysis. Figure 3 also shows that PHEVs offered reductions in petroleum energy use compared to regular hybrid electric vehicles (HEVs). More petroleum energy savings could be realized as the AER increased, except when the marginal grid mix was dominated by oil-fired power generation, such as the marginal mix estimated for the region covering New York. Similarly, more GHG emissions reductions could be realized at higher AERs, except when the marginal grid generation mix was dominated by oil or coal. Electricity from renewable sources realized the largest reductions in petroleum energy use and GHG emissions for all PHEVs as the AER increased.

Conclusions and Future Directions

Conclusions

- FC technologies for distributed power generation approaching or exceeding the DOE target electrical efficiency of 40% offer significant reduction in energy use and GHG emissions compared to combustion technologies and the U.S. grid generation mix.
- Application of the PEM FC to forklifts offers significant reductions in energy use and GHG emissions compared to ICE forklifts and battery-powered forklifts charged through U.S. grid power.
- PHEVs offer significant reductions in petroleum energy use and GHG emissions relative to a conventional ICE vehicle that uses gasoline.
- CHHP FCs offer significant reductions in energy use and GHG emissions compared to FCs and distributed combustion technologies for CHP applications.

Future Work

- Conduct fuel-cycle analysis of criteria pollutant emissions for distributed combustion technologies and various FC system technologies for CHP and CHHP generation.
- Examine benefits of waste-based fuel production pathways such as landfill gas and potentially biogas from waste water treatment plants.
- Incorporate the newly developed pathways into the public version of GREET.

FY 2009 Publications/Presentations

- Elgowainy, Amgad, Andrew Burnham, Michael Wang, John Molburg, and Aymeric Rousseau, 2009, *Well-To-Wheels Energy Use and Greenhouse Gas Emissions Analysis of Plug-in Hybrid Electric Vehicles*, ANL/ESD/09-2, Center for Transportation Research, Argonne National Laboratory, Argonne, IL, February.
- Elgowainy, Amgad, Andrew Burnham, Michael Wang, John Molburg, and Aymeric Rousseau, 2009, "Well-To-Wheels Energy Use and Greenhouse Gas Emissions of Plug-in Hybrid Electric Vehicles," 2009-01-1309, SAE World Congress.
- Elgowainy, A., L. Gaines, and M. Wang, 2009, "Fuel-Cycle Analysis of Early Market Applications of Fuel Cells: Forklift Propulsion Systems and Distributed Power Generation," *International Journal of Hydrogen Energy* 34(9): 3557–3570.
- Elgowainy, A., and M. Wang, 2008, *Fuel Cycle Comparison of Distributed Power Generation Technologies*, ANL/ESD/08-4, Center for Transportation Research, Argonne National Laboratory, Argonne, IL, November.

FIGURE 3. Summary of WTW Petroleum Energy Use and GHG Emissions for Combined Charge Depleting (CD) and Charge Sustaining (CS) Operations Relative to a Baseline ICE Gasoline Vehicle (GV)

5. Gaines, L., A. Elgowainy, and M. Wang, 2008, *Full Fuel-Cycle Comparison of Forklift Propulsion Systems*, ANL/ESD/08-3, Center for Transportation Research, Argonne National Laboratory, Argonne, IL, October.

VII.13 Evaluation of the Potential Environmental Impacts from Large-Scale Use and Production of Hydrogen in Energy and Transportation Applications

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Contract Number: DE-FC36-07GO17109

Project Start Date: September 28, 2007
Project End Date: September 27, 2009

Objectives

The purpose of this project is to systematically identify and examine possible long-term ecological and environmental effects from the production of hydrogen from various energy sources based on the DOE hydrogen production strategy and the use of that hydrogen in transportation and power applications. From these analyses, a comprehensive impact assessment will be developed to provide reliable estimates of hydrogen leakage rates to the environment and criteria pollutants emitted from the distributed and central-scale hydrogen systems that might be deployed in the future. The project will involve modeling, data analysis and field experiments. Specific objectives include analyses to address the following:

- Impact of hydrogen releases on the oxidative capacity of the atmosphere.
- Long-term stability of the ozone layer due to changes in hydrogen emissions.
- Impact of hydrogen emissions and resulting concentrations on climate.
- Impact on microbial ecosystems involved in hydrogen uptake.
- Role of biological impacts in causing indirect effects on the atmosphere and climate.
- Criteria pollutants emitted from distributed and centralized hydrogen production pathways.
- Criteria pollutants emitted given different scenarios of vehicle market penetration.
- Impact of criteria pollutants on human health, air quality, ecosystems and structures under different penetration scenarios.

Technical Barriers

This project addresses the following technical barriers from the Systems Analysis section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) Future Market Behavior
- (B) Stove-piped/Siloed Analytical Capability
- (C) Inconsistent Data, Assumptions and Guidelines
- (D) Suite of Models and Tools

Contribution to Achievement of DOE Systems Analysis Milestones

This project will contribute to achievement of the following DOE milestones from the Systems Analysis section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- **Milestone 11:** Complete environmental analysis of the technology environmental impacts for the hydrogen scenarios and technology readiness. (2Q 2015)

Accomplishments

- Completed development of emissions scenarios based on Intergovernmental Panel on Climate Change (IPCC) growth scenarios and different H₂ fuel cell technology adoption scenarios. These scenarios span a wide range of possible future paths and encompass the high and low IPCC growth scenarios. Combustion related emissions are evaluated for H₂ fuel cell and H₂ internal combustion engine (ICE) technology adoption. H₂ emissions are based on the conversion of all land-based transportation to H₂ fuel and assume a ~2.5% H₂ leakage rate.
- Preliminary Integrated Assessment Model calculations show substantial decreases in 2050 CO₂ radiative forcing and resulting climate effects from the reduction in CO₂ emissions in a fuel cell powered transportation sector when the H₂ is produced without carbon emissions.
- Stratospheric impact simulations are underway with preliminary results showing a 0.9% decrease in global stratospheric ozone for the highest H₂ emitting scenario. This is potentially a significant concern that needs further study. Though these simulations did not directly include the H₂ offset CO₂ reduction, previous published peer-reviewed studies indicate that this reduction will cause an additional slight decrease in stratospheric ozone.
- Tropospheric and regional impact model runs have been completed to evaluate effects on hydroxyl, tropospheric ozone, and other pollutants on surface air quality for these scenarios. For all future growth scenarios air quality metrics generally improve significantly with the H₂ fuel cell technology option (surface O₃ decreases by as much as 15 ppb for the high emissions scenario), however for the H₂ ICE technology option there is much less improvement in air quality (surface O₃ decreases by only 5 ppm).
- Analyses of measurements in Mexico City demonstrate cases of high H₂ concentrations in a current highly polluted urban atmosphere.

- New laboratory H₂ soil uptake studies show a significant non-linear enhancement of soil H₂ uptake with increasing atmospheric H₂ concentrations. This uptake enhancement could provide a large negative feedback on the growth of atmospheric H₂ concentrations expected from an hydrogen-based transportation sector. For the first time, such nonlinear effects are now being considered in new atmospheric impacts studies.
- H₂ embrittlement of metallic structures will not be significant from the expected levels of atmospheric H₂ under a hydrogen-based transportation sector.
- The risk due to oxygen release plumes from H₂ production has been evaluated. These plumes are not likely to be a problem.

Introduction

There is limited quantitative understanding of the projected market penetration, the changes in emissions avoided or gained upon transitioning to hydrogen-based systems, and on the resulting impacts on the environment. This project is aimed at an end-to-end analysis of the potential ecological and environmental impacts of transitioning to a hydrogen-based society. Our project team is composed of scientists, engineers, and economists that have the right blend of expertise and tools to appropriately attack the issues we will face in this assessment. The purpose of this project is to systematically identify and examine possible near and long-term ecological and environmental effects from the production of hydrogen from various energy sources based on the DOE hydrogen production strategy and the use of that hydrogen in transportation and power applications. This project, wherever possible, uses state-of-the-art numerical modeling tools of the environment and energy system emissions in combination with relevant new and prior measurements and other analyses to assess the understanding of the potential ecological and environmental impacts from hydrogen market penetration. Careful attention is being given to both H₂ technology options and market penetration scenarios developed by DOE, as well as other atmospheric trace gas projections such as the IPCC Special Report on Emissions Scenarios scenarios being used in climate analyses and the decline in halocarbons due to the Montreal Protocol following World Meteorological Organization. In the process, DOE will also be provided with a capability for further assessing current understanding and remaining uncertainties for addressing the potential environmental impacts from hydrogen technologies.

Approach

Using state-of-the-art modeling tools of the energy-technology-economy system along with other analyses, we are evaluating changes in emissions due to hydrogen technologies and uses. We evaluate the effects of hydrogen on climate and on all aspects of atmospheric chemistry and composition using state-of-the-art three-dimensional global and regional models of atmospheric chemistry and physics. Through field and laboratory studies, we will gain new insights into the relationships affecting soil uptake and the impacts on ecosystems. Analyses will be done, under various assumptions of hydrogen concentrations, of the effect of the potential of hydrogen to degrade materials and structures. From these separate but heavily coordinated assessment studies, a comprehensive impact assessment will be developed to provide reliable estimates of hydrogen leakage rates to the environment and criteria pollutants emitted from the distributed and central-scale hydrogen systems that might be deployed in the future.

Results

Scenarios of future emissions of greenhouse and other important atmospheric gases and particles have been developed encompassing different hydrogen technology adoption paths and future growth projections in transitioning to a hydrogen-based transportation sector. Future growth projections are based on the IPCC A1Fi and B1 scenarios which represent the continued heavy use of fossil fuels and a lower fossil fuel intensity path respectively. Two technology adoption paths were evaluated, the first utilizing hydrogen fuel cells in which volatile organic carbon (VOC), oxides of nitrogen (NO_x), and particulate emissions (PM) are reduced and the second representing a transitional scenario where hydrogen is burned in ICEs in which only VOC and PM emissions are reduced. In these scenarios we assumed all land-based transportation was converted to H_2 and an H_2 leakage rate of $\sim 2.5\%$. The A1Fi and B1 scenarios are the high and low range of the IPCC scenarios and in conjunction with the two technology adoption alternatives span a wide range of possible future paths.

Three-dimensional tropospheric and regional model simulations of the 2050 atmosphere constrained by the emission scenarios described above have been completed. Analyses of the results reveal that the atmospheric H_2 burden increases under all scenarios, by $\sim 40\%$ for A1Fi and by $\sim 25\%$ for B1. Substantial tropospheric O_3 decreases of 7% (A1Fi) and 5% (B1) are realized only for the fuel cell adoption scenarios, while O_3 decreases only slightly (1%) for the H_2 ICE technology scenarios. The oxidizing capacity of the troposphere, as indicated by the tropospheric OH burden, decreases for the fuel cell technology option by 4% for both the A1Fi and B1 scenarios but increases

with ICE technology by 6% in the A1Fi and 3% in the B1 scenarios respectively (Table 1). Atmospheric VOC and particulate concentrations decrease in all scenarios.

TABLE 1. Model simulated 2050 annual mean global tropospheric burdens of various gases. Data are for the A1Fi and B1 based emissions scenarios for the Base case (B), fuel cell technology adoption (HS2), and internal combustion technology adoption (HS3). Units are indicated in the column heads for the base scenarios and percent differences for the HS2 and HS3 scenarios.

Scenario	H_2 [ppb]	O_3 [ppb]	CO [ppb]	NO_x [ppt]	SO_2 [ppt]	OH [$1\text{e}^5/\text{cm}^3$]
A1Fi-B	830	44	132	99	44	9
A1Fi-HS2	+39%	-7%	-14%	-16%	-0.5%	-4%
A1Fi-HS3	+40%	-1%	-17%	11%	-1.4%	+6%
B1-B	577	38	90	60	39	10
B1-HS2	+25%	-5%	-4%	-11%	-0.3%	-4%
B1-HS3	+28%	-1%	-7%	+4%	-3.4%	+3%

For the A1Fi fuel cell technology scenario background annual mean surface O_3 decreases by $\sim 10\%$ and up to 50% over some regions (Figure 1). Over the continental U.S., July monthly average O_3 decreases by more than 20% along the coasts and by $\sim 10\%$ in the interior (Figure 2). $\text{PM}_{2.5}$ also decreases by $\sim 4\%$ over much of the U.S. with decreases of $\sim 20\%$ over parts of California and the Ohio River Valley (Figure 3). Decreases for the B1 scenario are similar in distribution but smaller in magnitude.

Preliminary results from the stratospheric impact studies show a 0.9% decrease in global stratospheric ozone for the highest H_2 emitting A1Fi scenario. Though these simulations did not directly include the H_2 offset CO_2 reduction, previous studies indicate that

FIGURE 1. Model simulated 2050 annual average percent change in surface ozone for the A1Fi scenario with fuel cell technology adoption (A1Fi-HS2) simulated with the CAM-Chem 3-dimensional global chemistry-transport model.

FIGURE 2. July average percent change in surface ozone over the continental U.S. for the A1Fi-HS2 scenario, simulated with the community multiscale air quality model (CMAQ).

FIGURE 3. July average percent change in $PM_{2.5}$ over the continental U.S. for the A1Fi-HS2 scenario, simulated with CMAQ.

this reduction will cause an additional slight decrease in stratospheric ozone.

Long-term exposure trials indicate that soil H_2 uptake increases with increasing ambient H_2 concentrations. This response could play an important role in determining future H_2 concentrations in a hydrogen economy as demonstrated by our initial studies. The functional dependence of the uptake enhancement has been refined and implemented in our 3-dimensional global tropospheric model. Based on H_2 atmospheric concentrations from our previous A1Fi simulations the uptake may be enhanced by a factor of 4. Full impact studies are underway.

Work on the integrated assessment model is underway. The CO_2 module is complete and analysis of the impact of the displaced CO_2 emissions from conversion to a hydrogen transportation sector indicate that 2050 CO_2 concentrations would be 47 ppm lower for the A1Fi scenario and 21 ppm lower for the B1 scenario. These differences correspond to reduced CO_2 radiative forcings of 0.5 W/m^2 and 0.2 W/m^2 for the A1Fi and B1 scenarios, respectively.

Conclusions and Future Directions

- The tropospheric and regional air quality impacts of an H_2 -fueled transportation sector are mostly positive, though for O_3 the impact depends critically on the technology adopted.
- Preliminary results suggest that H_2 causes a decrease in stratospheric O_3 . This is a potential concern. These studies and analysis are ongoing.
- The H_2 soil sink depends on the atmospheric H_2 concentration and will likely impact future H_2 concentrations. Further laboratory studies of enhanced H_2 soil uptake dependence on different parameters, e.g., soil type, temperature, and moisture are necessary.
- Global 3-dimensional modeling studies are underway to evaluate the impact of the H_2 adaptive soil sink on future atmospheric H_2 concentrations. The potential importance needs study.
- Reduced atmospheric CO_2 concentrations in an H_2 economy will decrease CO_2 radiative forcing. Development of the integrated assessment model is being completed and the climate impact of various H_2 emissions and adoption scenarios will be evaluated.
- Measurements of H_2 leaks in realistic conditions are badly needed.
- Field studies of total ecosystem response and soil sink as a function of climate parameters are needed.

FY 2009 Publications/Presentations

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2. Olsen, S., D. Wuebbles, D. Wang, W. Jia, and A. Rockett, (2008), Climate and Air Quality Impact of a Hydrogen Economy, Eos Trans. AGU, 89(53), Fall Meet. Suppl., Abstract A21B-0146, Fall American Geophysical Union Meeting, San Francisco, CA, 2008.
3. Dubey M.K., Rahn, T., Olsen, S., and Mazzoleni, C.; The Hydrogen Cycle in Mexico City: Tracing traffic patterns, fingerprinting sources & holiday effects, in preparation for *Atmos. Chem. & Phys.*, 2009.

4. Dubey, M.K., Horowitz, L. et al. Impacts of Global Hydrogen Economy on Air Quality, Oxidative Capacity, and Stratospheric Ozone: MOZART simulations, in preparation for *Int. Journal of Hydrogen Economy*, 2009.
5. Olsen, S., presentation at 2009 DOE Hydrogen Program Annual Merit Review and Peer Evaluation Meeting.

VII.14 Potential Environmental Impacts of Hydrogen-Based Transportation and Power Systems

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- Stanford University, Palo Alto, CA
- Potomac-Hudson Engineering, Bethesda, MD

Project Start Date: September 26, 2007

Project End Date: September 25, 2009

Objectives

The overall goal of the project is to compare emissions of hydrogen, the six criteria pollutants (CO, SO_x, NO₂, particulate matter, ozone, and lead), and greenhouse gases from near- and long-term methods of generating hydrogen for vehicles and stationary power systems, and the effects of those emissions on climate, human health, the ecosystem, and structures. The specific objectives are as follows:

- Develop market penetration scenarios for hydrogen. Each scenario will include emission rates of hydrogen including leakage; emissions of the six criteria pollutants, volatile organic compounds (VOCs), and greenhouse gases for each technology used for production of hydrogen; and the timeframe for shifting vehicles and stationary power systems to hydrogen.
- Predict changes in atmospheric concentrations of hydrogen and other constituents in the troposphere and stratosphere.
- Quantify near and long-term effects on air quality, human health, ecosystems, and structures using model output and accepted health and ecosystem effect levels and ambient air criteria.

- Identify other more subtle effects of shifting to a hydrogen-based economy.

Technical Barriers

This project addresses the following technical barriers from the Systems Analysis section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) Future Market Behavior
- (C) Inconsistent Data, Assumptions and Guidelines
- (E) Unplanned Studies and Analysis

Contribution to Achievement of DOE Systems Analysis Milestones

This project will contribute to achievement of the following DOE milestone from the Systems Analysis section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- **Milestone 11:** Complete environmental analysis of the technology environmental impacts for the hydrogen scenarios and technology readiness. (2Q, 2015)

Accomplishments

The capabilities of the Gas, Aerosol, Transport, Radiation, General Circulation, Mesoscale, and Ocean Model (GATOR-GCMOM) soil routine have been extended to mechanistically represent hydrogen loss to soils. The total surface resistance term was generalized to include separate treatment of the vegetated and non-vegetated soil fractions. Resistance to soil uptake was parameterized in terms of deposition velocities appropriate for grasslands, forests, savannah, and agricultural lands (subdivided into two seasons). Soil moisture limitation and soil temperature corrections were included. For deserts, the uptake rates were scaled from uptake rates for forests by adjusting the soil organic carbon content as appropriate between the two biomes. Maximum uptake rates were based on laboratory experiments conducted under conditions that were non-limiting for either soil moisture, temperature, or organic carbon. The total soil uptake was then calculated by multiplying the maximum rate by each limiting factor.

- Using the Greenhouse gases, Regulated Emissions and Energy use in Transportation (GREET) Model,

developed emissions for transportation in baseline years and for two scenarios in 2030 and 2050 using population, vehicle ownership rates, and other data consistent with the Intergovernmental Panel on Climate Change (IPCC) A1B cases for the U.S., Western Europe, Canada, Australia, China, Japan, New Zealand, and South Korea. The two scenarios included hydrogen fuel cell vehicles (HFCVs) produced using the range of methods specified below in the Results section. Sensitivity analyses were also conducted to compare alternative ways of producing hydrogen for the vehicles.

- Completed initial runs of the GATOR-GCMOM model for baseline 2000 and IPCC Scenario A1B with 90% HFCVs in developed countries and 45% HFCV penetration in other countries and where the hydrogen is produced by steam reforming of natural gas. These results were compared with recent simulation results in which the world's fossil-fuel onroad vehicles (FFOVs) are converted to HFCVs and where the hydrogen is produced by wind-powered electrolysis.

Introduction

The goal of this project is to analyze the effects of emissions of hydrogen, the six criteria pollutants and greenhouse gases on climate, human health, ecosystems, and structures. Initial concerns with the adoption of a hydrogen economy have focused on possible effects of hydrogen releases to the atmosphere. Modeling results of Tromp et al. [1], predicted significant ozone (O_3) depletion and moisture increases in the stratosphere. The projected additional moisture was hypothesized to cause stratospheric cooling and increased formation of polar ice clouds that indirectly catalyze ozone destruction. Whereas O_3 is a problem in the troposphere causing medical, ecological, and material problems, in the stratosphere O_3 protectively absorbs ultraviolet radiation and protects the earth surface from bond breaking energy that can lead to health maladies such as skin cancer. However, numerous researchers were quick to note two major problems with the modeling and analysis presented in Tromp et al. [1]: 1) the projected H_2 leakage rates assumed were very high (i.e., 10 to 20 percent of production versus 1 to 3 percent projected by other investigators), and 2) the paper did not incorporate the decreases in CO_2 and priority pollutants that would accompany the shift to hydrogen. It is known that hydrogen can escape containment at rates about four times that of equally compressed air. Still, Tromp et al.'s assumed leakage rates were about a factor of ten times larger than those calculated by other investigators.

Approach

There are five elements associated with the overall technical approach:

- Develop market penetration scenarios for hydrogen.** Each scenario includes emission rates of hydrogen, including leakage, emissions of the six criteria pollutants, VOCs, and greenhouse gases, for each technology used for production, the mix of technologies used, and the timeframe for shifting vehicles and stationary power systems to hydrogen.
- Predict changes in atmospheric concentrations of hydrogen and other constituents.** The GATOR-GCMOM model developed by Mark Jacobson at Stanford University is being used to predict tropospheric and stratospheric concentrations of gases and aerosols.
- Extend the GATOR-GCMOM soils module.** The dominant sink for H_2 in the troposphere is loss to soils. This accounts for about 80 percent of the total H_2 sink [2]. The capabilities of the GATOR-GCMOM soil routine have been extended to mechanistically represent hydrogen loss to soils.
- Quantify near and long-term environmental effects.** The effects on air quality, human health, ecosystem, and building structures will be quantified using model output and accepted health and ecosystem effects levels, and ambient air quality criteria.
- Identify other more subtle effects of shifting to a hydrogen-based economy.**

Results

The study team has identified two emission scenarios, for which we have quantified the emissions of hydrogen and six criteria pollutants, VOCs, and greenhouse gases. These scenarios are based on the U.S. hydrogen transportation scenarios per Greene et al. [3]. These scenarios are depicted in Figure 1. The emissions analysis used values derived from GREET 1.8 [4]:

- Scenario 1:** (20% Fuel Cell Vehicles [FCVs] in 2030 and 90% FCVs in 2050). Assuming hydrogen production from steam reforming of natural gas in 2030 and from the no carbon policy source mix for 2050: Biomass without sequestration 5%; Coal gasification without sequestration 66%; Steam reforming using natural gas 28%; Renewable energy 1%.
- Scenario 2:** (50% FCVs in 2030 and 95% FCVs in 2050). Assuming hydrogen production from steam reforming of natural gas in 2030 and from the carbon policy source mix for 2050: Biomass without sequestration 42%; Coal gasification with sequestration 45%; Steam reforming using natural gas 10%; Renewable energy 3%. The percent

FIGURE 1. Vehicle Penetration and Stationary Source Scenario Options

using natural gas was reduced by 2 percent and added to renewables, given the large increase in wind capacity that occurred in 2007 and that is envisioned for 2030.

Emission estimates were also developed for Western Europe and six other countries.

Emission factors were developed using GREET for HFCVs for comparison to hybrids, gasoline, and diesel vehicles. The percent decrease in emissions with HFCVs was determined by the model for the 2030 and 2050 cases. The 2050 results showed that NO_x, NO₂, CO, CO₂, and CH₄ would decrease, which is consistent with the preliminary results for GATOR-GCMOM. VOCs showed a decrease as a group based on the GREET results, although the specific results by chemical showed some increases in the GATOR-GCMOM results.

The GATOR-GCMOM model, which solves dynamical, gas, aerosol, cloud, transport, radiation and surface processes [5-7] was used to simulate the effects of converting the world's FFOVs to HFCVs, where the H₂ is produced by steam reforming of natural gas. Only the preliminary results after 1.5 years of the IPCC 2050 A1B simulation are available, but the results indicate that the conversion to 95% HFCVs in the developed countries and 45% HFCV penetration in other countries will result in reduced emissions of CO₂, CO, NO_x, aldehydes, and black carbon. A sample of the preliminary results for the atmospheric differences in ambient concentrations between the 2050 A1B base case and the conversion to HFCVs are in shown in Figure 2. Natural gas-HFCVs increased H₂ slightly, decreased CO₂ and CO, and increased ocean pH. These model simulations are still underway and will be extended to 10-year simulations to achieve study-state results.

These initial results are consistent with recent GATOR-GCMOM simulations of the conversion of the world's FFOVs to HFCVs, where the H₂ is produced by wind-powered electrolysis [8]. For the comparison of the same IPCC scenarios over 10 years, the conversion to HFCVs were calculated to reduce tropospheric CO ~5%, NO_x ~5-13%, most organic gases ~3-15%, OH ~4%, ozone ~6%, and peroxyacetyl nitrate ~13%, but to increase CH₄ ~4% due to the lower OH. Lower OH also increased upper tropospheric-lower stratospheric ozone, increasing its global column by ~0.25%. For the case of the wind-powered electrolysis production of H₂, the simulation results indicate that conversion to HFCVs will not adversely affect tropospheric pollution or the stratospheric ozone layer.

Conclusions and Future Directions

This project has been underway for almost two years and has made significant progress on the five primary objectives. In the final three months we will focus on the following efforts:

- Completion of the GATOR-GCMOM model simulations and the interpretation of the results.
- The quantification of the effects of implementing the selected market penetrations scenarios will examine potential effects in these five areas:
 - Climate: air temperature, cloud production, ozone levels, photochemical smog.
 - Human health: six criteria pollutants, lead, greenhouse gases compared to health-effect levels and national ambient air quality standards.

FIGURE 2. Preliminary results from GATOR-GCMOM simulation of the 2050 IPCC A1B. Scenario with 90% HFCVs in developed countries and 45% HFCV penetration in other countries.

- Ecosystems: use effects levels for criteria pollutants and greenhouse gases to evaluate impacts on aquatic and terrestrial biota.
- Structures: effects of acids, ozone, particulate matter, and greenhouse gases on materials, buildings, structures, historical sites, roadways.
- Other environmental effects: e.g. mining and processing of trace metals used as catalysts or in photovoltaic cells.

FY 2009 Publications/Presentations

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2. DOE 2009 Annual Merit Review & Peer Evaluation. Washington, D.C. May 19, 2009.

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6. Jacobson, M.Z. 2006. Effects of absorption by soot inclusions within clouds and precipitation on global climate. *J. Phys. Chem.* 110:6860-6873.
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8. Jacobson, M.Z. 2008. Effects of wind-powered hydrogen fuel cell vehicles on stratospheric ozone and global climate. *Geophys. Res. Lett.* 35, L19803.

VII.15 Pathways to Commercial Success: Technologies and Products Supported by the Hydrogen, Fuel Cells & Infrastructure Technologies Program

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Project Start Date: August 1, 2007
Project End Date: September 30, 2009

Development and Demonstration Plan. However, it supports the following subtask in Table 4.6.1: “Provide other support to the program and other organizations” (under Task 3).

Accomplishments

- Produced a report entitled, “*Pathways to Commercial Success: Technologies and Products Supported by the Hydrogen, Fuel Cells & Infrastructure Technologies Program*,” describing patents, commercialized technologies, and emerging technologies that have emerged from the HFCIT Program and its predecessor programs.
- Updated the HFCIT technology tracking database containing information on commercial and emerging technologies.

Objectives

This objective of this project is to provide a retrospective assessment of Hydrogen, Fuel Cells & Infrastructure Technologies (HFCIT) Program benefits by tracking commercial successes of HFCIT-developed technologies (and technologies developed by HFCIT predecessors) and estimating the business impacts, when possible. Tracking technologies helps determine the impacts of research and development (R&D) undertaken by the program, develop lessons learned, and guide future program developments. Technology tracking also allows for more effective management of R&D programs and budget defense, and the database developed serves as the institutional memory for the program.

Technical Barriers

This project addresses the following technical barriers from the Systems Analysis section (4.5) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (C) Inconsistent Data, Assumptions and Guidelines
- (E) Unplanned Studies and Analyses

Contribution to Achievement Systems Analysis Milestones

This project does not contribute to achievement of any specific milestones listed in the Systems Analysis section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research,

Introduction

The HFCIT Program and its predecessor programs have been conducting a wide range of hydrogen and fuel cell R&D projects, some of which have resulted in patents and/or products now available in the commercial marketplace. This project focused on identifying and describing both patents and commercialized technologies resulting from Energy Efficiency and Renewable Energy (EERE) hydrogen and fuel cell program activities, as well as technologies likely to be commercialized in the near future (called “emerging” technologies).

Once they were identified, Pacific Northwest National Laboratory (PNNL) gathered information on the commercialization status of EERE-developed hydrogen and fuel cell technologies that are on the market, and, when possible, quantified the business impacts (e.g., number of units sold) of these successfully commercialized technologies. Working with the technology vendors, PNNL documented product characteristics, history, applications, capabilities, and benefits.

Approach

To identify and document the commercial and near-commercial (emerging) hydrogen and fuel cell technologies and products that benefited from EERE support, PNNL undertook several efforts simultaneously. The first effort was a patent search and analysis to

identify hydrogen and fuel cell related patents that are associated with HFCIT-funded projects (or projects conducted by DOE-EERE predecessor programs) and to ascertain the patents' current status, as well as any commercial products that may have used the technology documented in the patent.

The second effort was a series of interviews and document reviews to identify and characterize commercial and emerging technologies that have directly benefited as a result of direct funding from the HFCIT Program (or funding from EERE predecessor programs) or from grants under programs such as the Small Business Innovation Research and Small Business Technology Transfer.

Data gathered about the technologies were then entered into a HFCIT Program Technology Tracking Database, a Lotus Notes database that is updated and available on the DOE system. For each of the commercial and emerging hydrogen technologies in the database, a summary description was prepared, edited, and sent it to the industry/research organization point of contact for review and subsequent approval before sending it to HFCIT Program personnel to review.

Results

The first effort for this task, the patent search and analysis, identified 144 patents: 74 fuel cell patents, 49 production/delivery patents, and 21 storage patents. Figure 1 shows the patents awarded in each year, starting with pre-1997 patent awards through 2007. As the figure shows, 2001 and 2006 had significantly more patents than the other years because those were the top award years for both the fuel cell and production/delivery patents. The storage patent awards are spread out over the entire period, with a peak of four awards in 2004.

Three types of organizations received the patents: national laboratories (69 patents), private companies (56 patents), and universities (19 patents). The national laboratories had patent awards for fuel cell and production/delivery technologies that were almost equal to those awarded to private companies in these two areas. The national laboratories had 62% of the awards in the storage area. While the universities received fewer total patent awards, they had 74% of their patents in the production/delivery area.

The national laboratories and private companies both received more than half of their patents in the fuel cell area.

Figure 2 shows the patent award status by use. As the figure shows, three patents are used in commercial products and 19 are part of research now taking place on emerging technologies identified on the technology tracking list compiled. In addition, 34 awarded patents are still being used in research that is more than three years from a commercial product. Of the 118 patents reviewed, 52% are no longer being used in research. This was particularly true in the fuel cell area, where 43 of the 60 patents (72%) are no longer being used in research.

FIGURE 1. Number of Patents Awarded Over Time

FIGURE 2. Status of Awarded Patents

research. However, this is not true in the storage or production/delivery area, where the patents are still being used in research.

The second effort for this task, identifying the commercial and emerging technologies and tracking results, found 18 commercial technologies and 40 emerging technologies. Figure 3 shows the number of commercial technologies on the market. Years 2000 – 2006 showed a steady addition of technologies entering the market of one to three per year. In 2007 four technologies entered the market, and in 2008 three technologies have done so. Figure 4 shows the distribution of technologies in the HFCIT research areas. As shown, an almost equal number of emerging technologies occurred between the fuel cell and production/delivery areas, with the storage area having only 23% as many emerging technologies.

A total of 40 emerging and 18 commercial technology descriptions were prepared and included in the report.

Conclusions and Future Directions

Commercialization of technologies that were cultivated in a government R&D program is generally viewed as a measure of success. In addition, technology tracking can support:

- Effective management of R&D programs
- Budget defense
- Strategic planning
- Portfolio management
- Institutional memory

The report and technology tracking database will help organizations highlight the impacts and benefits of their products, potentially expanding their markets. It will also help publicize emerging technologies to interested commercialization partners.

The information presented on commercial and emerging technologies fulfills the primary objective – to assess the commercialization status of EERE-developed hydrogen and fuel cell technologies and provide information on the business impacts. Insights about pathways to successful introduction of hydrogen and fuel cell technologies are beginning to emerge from this analysis, but this topic has not yet been fully explored.

FIGURE 3. Cumulative Number of Commercial Technologies on the Market

FIGURE 4. Distribution of Emerging HFCIT Technologies

FY 2009 Publications/Presentations

1. Pacific Northwest National Laboratory, *Pathways to Commercial Success: Technologies and Products Supported by the Hydrogen, Fuel Cells & Infrastructure Technologies Program*, draft report to the U.S. Department of Energy Hydrogen, Fuel Cells & Infrastructure Technologies Program, September, 2008.
2. Weakley, S.A., M. Placet, "Pathways to Commercial Success: Technologies and Products Supported by the HFCIT Program," a poster session at the Hydrogen Annual Merit Review, Washington, D.C., May 18, 2009.

VII.16 DOE Hydrogen Program Risk Analysis in Support of EERE's Portfolio Analysis

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Contribution to Achievement of DOE Systems Analysis Milestones

This project will contribute to achievement of the following DOE milestones from the Systems Analysis section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- **Milestone 7:** Complete an analysis of the hydrogen infrastructure and technical target progress for the hydrogen fuel and vehicles. (2Q, 2011)
- **Milestone 8:** Complete analysis and studies of resource/feedstock, production/delivery and existing infrastructure for technology readiness. (4Q, 2014)
- **Milestone 10:** Complete an analysis of the hydrogen infrastructure and technical target progress for technology readiness. (2Q, 2015)

Objectives

- **Near Term:** Provide risk analysis methodologies and tools that are useful to staff, team leaders, program managers, and portfolio managers in identifying, quantifying, evaluating, managing, monitoring, documenting, and communicating technology development risks and benefits.
- **Long Term:** Assist project, program, and portfolio decision-making that aligns and balances the DOE Office of Energy Efficiency and Renewable Energy's (EERE's) portfolio with strategic goals.

Technical Barriers

This project addresses the following technical barrier from the Systems Analysis section of the Hydrogen, Fuel Cells and Infrastructure Technologies (HFCIT) Program Multi-Year Research, Development and Demonstration Plan:

(E) Unplanned Studies and Analysis

In addition, this project addresses the following technical barriers from the Systems Integration section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (B) Adapting System Integration Functions to an R&D Program
- (C) Inherent Uncertainty in R&D

Accomplishments

- Analyzed uncertainty associated with future technical progress for fuel cells, on-board storage, and several hydrogen production and associated technologies (including compression, storage, and dispensing for distributed hydrogen production).
- Assessed expert opinions on potential technical progress for three funding scenarios: without DOE funding, with planned DOE funding, and with expanded DOE funding.

Aggregated individual expert opinions and projected potential progress for the three funding scenarios including a projection for optimum technology selection between comparable on-board storage technologies.

- Provided projections to be used in EERE's portfolio analysis.

Introduction

As part of its portfolio analysis, EERE required all of its programs to perform an uncertainty analysis around technical performance measures (TPMs). That uncertainty analysis is commonly referred to as the "Risk Analysis." It involves assessing expert opinions regarding future status of the TPMs in stochastic form (i.e., as a probability density function – pdf) and combining individual projections from multiple experts to generate a single aggregated projection. The

aggregated projections are then used in market and economic analysis models to estimate future levels of hydrogen penetration and the resultant effects on emissions (primarily greenhouse gases), oil imports, and economics.

EERE plans to use the results to conduct a more robust portfolio analysis of all its programs and options. The HFCIT program will also use the results to understand potential tradeoffs between objectives and how the overall objective (enabling the hydrogen economy) may be met even though some of the technical targets may not be (other targets may be exceeded). In addition, the HFCIT program gains a better understanding of the probability of reaching the technical targets at different funding levels and can use that information in making decisions on how to adjust funding allocations.

Approach

The following approach was used for all three technology areas (production, on-board storage, and proton exchange membrane [PEM] fuel cells):

- Identify technology improvement opportunities (TIOs). These are research areas where success might improve technology performance (e.g., improved reactor design for production or cryo-compressed on-board storage).
- Select and characterize TPMs. These are measurements of performance (e.g., yield and capital cost).
- Select experts to participate.
- Experts estimate future TPM potential (stochastic estimation):
 - Meeting to explain the process, discuss assumptions, and elicit feedback.
 - Aggregation of initial responses.
 - Present initial responses to experts and allow them to discuss their input.
 - Experts modify responses as desired.
 - Aggregation of final responses.
- Provide TPM potential results as input to additional models for use in EERE's portfolio analysis.

Results

Hydrogen Production and Distribution

The following four TIOs were included in this year's uncertainty analysis:

- central biomass gasification,
- central wind-powered electrolysis,
- distributed ethanol reformation, and

- compression-storage-dispensing (CSD) at the distribution station.

For all three production TIOs, the following TPMs were projected:

- efficiency,
- capital cost, and
- operating and maintenance cost projections.

In addition, capacity factor was projected for central biomass gasification and distributed ethanol reformation, and labor cost was projected for central biomass gasification. For CSD, electricity input (a measure of efficiency) and capital cost were the only TPMs. Seven to eight experts provided input on each of the TIOs.

The experts' distributions were aggregated and the results were provided in vingtile-form to EERE staff for use in their portfolio analysis. Figure 1 shows results of the analysis of central biomass gasification. That figure has the efficiency projections and total capital cost projections for both zero DOE funding (labeled as "Baseline") and flat DOE funding (labeled as "Planned R&D"). The 10th percentile, 50th percentile, mode, and 90th percentile of the aggregated projection are shown on the figure for the selected goal (target) years (current, 2015, and 2025).

On-Board Storage

The following seven TIOs were included in this year's uncertainty analysis:

- 350 bar compressed gas
- 700 bar compressed gas
- Liquid
- Cryo-compressed
- Adsorbents
- Metal hydrides
- Chemical hydrides

For all seven TIOs, the following TPMs were projected:

- Gravimetric capacity
- Volumetric capacity
- Cost

assuming all other necessary technology improvements are achieved.

An objective function was developed to weigh tradeoffs among weight, volume, and cost assuming that the upstream (off-board) costs for those technologies are similar. Five of the technologies were optimized stochastically to develop a best or optimum scenario – a selection of best technologies based on distributions

FIGURE 1. Central Biomass Gasification Efficiency and Total Capital Cost Projections

FIGURE 2. 2015 System Cost pdfs Showing the Optimum Cost as Calculated Using the Objective Function

(i.e., no single winner). The resulting cost pdf for 2015 with a flat DOE budget is shown in Figure 2 with the corresponding pdfs for the five individual technologies. Note that the “Optimum” pdf has a higher percentage of low-cost results (less than \$5/kWh than any of the individual technologies). That is the case because the best technology was chosen for each of the many potential futures that were simulated in the stochastic analysis. Gravimetric capacity and volumetric capacity results are available upon request. The optimum results for each budget scenario and year were provided to the Powertrain Systems Analysis Toolkit team.

Fuel Cells

Only PEM fuel cells were considered for this analysis. The following TPMs were projected by as many as eight experts:

- System specific power (W/kg)
- System power density (W/L)
- Total fuel cell system cost (\$/kW)
 - 80 kW stack cost (\$/kW)
 - Power density (mW/cm²)
 - Platinum loading (mg/cm²)
 - Membrane cost (\$/m²)
 - Gas diffusion layer cost (\$/m²)
 - Gaskets (\$/kW)
 - Bipolar plate stamping (\$/kW)
 - Balance-of-plant costs (\$/kW)
 - Mounting frames (\$/kW)
 - Air loop (\$/kW)
 - Humidifier and water recovery loop (\$/kW)
 - Coolant loop (\$/kW)
 - Fuel loop (\$/kW)
 - System controller and sensors (\$/kW)
 - Other (\$/kW)

Aggregated system total cost results are shown in Figure 3.

FIGURE 3. PEM Fuel Cell System Cost Projections

Conclusions and Future Directions

Projections of potential technical improvement are important in helping the program prioritize research funding and in helping EERE manage its portfolio. Data generated by this project will be used for both purposes.

Risk analysis will probably be requested by EERE on a biennial basis. In the future, the focus may be on subsystem-level TPMs to improve understanding of each system's drivers and uncertainty to help focus research funding.

VII.17 Thermodynamic, Economic, and Environmental Modeling of Hydrogen (H₂) Co-Production Integrated with Stationary Fuel Cell Systems (FCS)

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Project Start Date: January 15, 2009
Project End Date: September 30, 2015

the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- **Milestone 5:** Complete analysis and studies of resource/feedstock, production/delivery and existing infrastructure for various hydrogen scenarios. (4Q, 2009)
- **Milestone 8:** Complete analysis and studies of resource/feedstock, production/delivery and existing infrastructure for technology readiness. (4Q, 2014)
- **Milestone 11:** Complete environmental analysis of the technology environmental impacts for the hydrogen scenarios and technology readiness. (2Q, 2015)
- **Milestone 26:** Annual model update and validation. (4Q, annually)
- **Milestone 41:** Annual Analysis Conference for the hydrogen community. (4Q, 2008; 4Q, 2009; 4Q, 2010; 4Q, 2011; 4Q, 2012; 4Q, 2013; 4Q, 2014; 4Q, 2015)

Objectives

This work develops multi-disciplinary models of novel stationary fuel cell system (FCS) designs that co-produce hydrogen (H₂-FCS). The two main objectives of this work are to

- Develop novel H₂-FCS designs that release low greenhouse gas emissions, and
- Develop novel H₂-FCS designs with low H₂ production cost.

Technical Barriers

This project addresses the following technical barriers from the Systems Analysis section (4.5) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) Future Market Behavior
- (B) Stove-piped/Siloed Analytical Capability
- (D) Suite of Models and Tools

Contribution to Achievement of DOE Systems Analysis Milestones

This project will contribute to achievement of the following DOE milestones for Systems Analysis within

Accomplishments

A. Develop and apply integrated engineering, economic, and environmental optimization and analysis models

- Developed preliminary, alpha version integrated optimization models that show the economic and environmental advantages of H₂-FCS compared with competing separate generators for electricity, heat and H₂.
- Completed case studies showing the benefits of installing H₂-FCS for electricity, heat and H₂ consumers, FCS manufacturers, and the environment.
- Demonstrated that global carbon dioxide (CO₂) emissions are lowest with our approach of implementing H₂-FCS with electrical and thermal networking, variable heat-to-power ratio, variable H₂-to-heat ratio, first load-following heat, and then load-following H₂ (for the case studies explored). Less fuel energy content is wasted when these approaches are used. This approach achieves a reduction in CO₂ emissions of over 40%.
- Demonstrated for the case studies explored that global costs are lowest with our approach of implementing H₂-FCS with electrically and thermally networking, variable heat-to-power ratio, variable H₂-to-heat ratio, maximum electrical

output, and then load-following both heat and H₂ in order of their relative expense. For a \$4.00/kg market H₂ price, this approach achieves a cost savings of 10%.

- Showed that our novel H₂-FCS designs have the lowest CO₂ emissions and costs of any H₂ production method.

B. Develop and apply thermodynamic and chemical engineering models for analyses of complete FCSs

- Developed preliminary, alpha version analytical and chemical process plant engineering models to analyze the quantity of H₂ that can be co-produced with electricity from an auto-thermal FCS, requiring no additional fuel consumption for combustion heating of endothermic processes.
- Derived, from fundamental thermodynamics, that such an idealized one Megawatt electric (MWe) FCS can be designed to make between ~150 and 450 kg H₂/day, which is enough H₂ to fuel between 220 and 660 H₂ fuel cell cars per day with no added CO₂ emissions from fuel combustion for reformation processes.¹
- Calculated the theoretical maximum of H₂ co-production as a function of fuel consumption, electrical work output, internal reuse of heat, inlet fuel and oxidant conditions, fuel and oxidant quantity, fuel type (natural gas and biogas), fuel cell stack and reformer operating temperature, and fuel cell current density.
- Verified analytical thermodynamic models against chemical process plant engineering models in Aspen Plus®.

C. Develop and apply chemical engineering models for analyses of hydrogen separation and purification sub-systems

- Developed preliminary, alpha version chemical engineering process plant models of hydrogen separation unit (HSU) sub-systems coupled to FCSs.
- Conducted scenario analyses to evaluate different HSU sub-system designs and cycle configurations.
- Compared and contrasted two different HSU sub-system designs, referred to here as HSU 1 and HSU 2, that include anode offgas heat recovery for displacing heat recovery from combustion of anode off-gas H₂, water-gas shift reactors (WGSRs) for shifting carbon monoxide (CO) and water (H₂O) into CO₂ and H₂, and compression and heat exchange to required pressure swing adsorber (PSA) inlet pressures and temperatures.
- Demonstrated a superior design called HSU 1, which recovers 73% of the available thermal energy, with a compressor load of 11% of gross power, and

increases the H₂ yield by 132% to 254 kg H₂/day (compared with a base case design with no heat recovery or WGSR that yields 110 kg H₂/day.)

- Developed a further refined design called HSU 2, which recovers 73% of the available thermal energy, with a compressor load of only 7% of gross power, and increases the H₂ yield by 172% to 298 kg H₂/day while also achieving neutral net water balance (compared with the base case design.)

Introduction

A. Develop and apply integrated engineering, economic, and environmental optimization and analysis models

In this first of three distinct modeling efforts, we developed integrated engineering, economic, and environmental models to optimize the design, installation, and control strategy of H₂-FCS for a particular location. To help achieve the DOE Hydrogen Program's goals of H₂ production with low fuel consumption and CO₂ emissions and to help meet System Analysis Milestone 11, the model minimizes global CO₂ emissions or global costs for the provision of electricity and heat to building owners, and H₂ to vehicle owners, from any combination of generators (including H₂-FCS.)

B. Develop and apply thermodynamic and chemical engineering models for analyses of complete fuel cell systems

In this second of three distinct modeling efforts, we derive the theoretical upper bounds for cost savings, fuel savings, and the quantity of H₂ co-production with H₂-FCS. High-temperature FCSs such as solid oxide fuel cells (SOFC) and molten carbonate fuel cells (MCFC) generate heat and unconsumed H₂ fuel that can potentially be recycled for H₂ co-production. This work evaluates the amount of H₂ that can be co-produced under idealized system configurations.

C. Develop and apply chemical engineering models for analyses of hydrogen separation and purification sub-systems

In this third of three distinct modeling efforts, we model the thermodynamics of the overall H₂ separation sub-system using detailed chemical engineering simulations in Aspen Plus®. A 1 MWe MCFC system, based on a similar product from FuelCell Energy (FCE), Inc., is thermally integrated with an HSU. PSA is evaluated as the H₂ separation technology due to its commercial readiness. We conduct a scenario analysis of different HSU designs, and report results for two

¹ http://www.fueleconomy.gov/feg/fcv_sbs.shtml

different designs (HSU 1 and HSU 2), compared to a baseline configuration.

Approach

A. Develop and apply integrated engineering, economic, and environmental optimization and analysis models

In this first of three distinct modeling efforts, our integrated engineering, economic, and environmental model evaluates a combination of novel operating strategies for the design, installation, and control of H₂-FCS. For each novel strategy, the model minimizes total yearly electricity, heat, and H₂ costs or CO₂ emissions by changing the installed capacity of the H₂-FCS. Our model considers a particular location's climatic region, building load curves, FCS type, and competitive environment. The model shows trade-offs between cost savings to building owners and H₂ consumers, CO₂ emission reductions, and fuel cell manufacturer sales. A FCS's load-following controls will match the hourly demand if it is within the physical constraints of the system. All demand not supplied by the FCS is purchased from competing electricity, heat, and H₂ generators. Our model focuses on H₂-FCS designs that reuse heat from the FCS to provide heat for the endothermic steam methane reforming (SMR) process for H₂ production such that no additional fuel need be consumed. Consequently, heat generated by the fuel cell can be used either for building heating or for producing more H₂ fuel. The model leaves tunable the ratio of recovered heat for buildings to H₂ fuel. For the case studies evaluated here, the competing H₂ generators are stand-alone SMRs and the H₂-FCS are assumed to be connected to the grid, allowing them to sell back unused electricity at retail market prices (i.e., net metering). The model assumes that H₂ production is for just-in-time use with no H₂ storage, is limited at 5% of the total fuel energy entering the system, and the additional H₂ production and separation equipment results in a 25% increase in fixed costs over the standard FCS without H₂ co-production. The lowest cost strategies combine electrical and thermal networking, a variable heat-to-electric power ratio, a variable H₂-to-heat ratio, maximum electrical output, and then H₂ and heat load-following.

B. Develop and apply thermodynamic and chemical engineering models for analyses of complete FCSs

In this second of three distinct modeling efforts, we developed a high level analytical approach for benchmarking the quantity of H₂ co-production available from high-temperature FCSs. Sandia focused on FCS designs with no marginal increase in fuel consumption or greenhouse gas emissions from combustion of the primary feedstock fuel for providing

heat for the endothermic fuel reforming processes. Sandia derives the theoretical limit of H₂ co-production from electrochemical heat production alone. The methodology involves hypothetically partitioning fuel cell stack heat into two quantities: (A) a quantity that meets the minimum energy requirement to provide heat to reform fuel solely to run the stack, and (B) a quantity that is potentially available to produce additional H₂. The steam reforming reactions can provide H₂ (A) for electrochemical conversion in the fuel cell anode compartment or (B) for H₂ co-production. For benchmarking an H₂ co-producing system against a standard system, we analytically separate the two processes – (A) and (B) -- in two “virtually” separate steam reformers – Reformer “A” (REFA) and Reformer “B” (REFB). REFA produces enough H₂ for the fuel cell to produce electric power. REFB produces H₂ as a separate product (for vehicles, etc.) Following this methodology, we calculated the theoretical maximum of H₂ co-production as a function of a) fuel consumption, b) electrical work output, c) ideal and non-ideal system-wide heat transfer for internal reuse of heat, d) inlet fuel and oxidant conditions, e) fuel and oxidant quantity, f) fuel type (natural gas and biogas from waste water treatment plants), g) fuel cell stack and reformer operating temperature, h) fuel cell current density, i) ideal and non-ideal fuel cell operation, and j) different levels of fuel cell voltage losses (polarizations). The models use polarization expressions and constants from the peer-reviewed literature and from industry. Figure 1 shows example data for such expressions; SOFC polarization and power density curves are plotted as a function of fuel cell operating temperature. This conceptual model is analyzed theoretically through thermodynamic and chemical engineering models using Aspen Plus® software.

Sandia conducts scenario analyses to determine the effects of changes in fuel cell operating conditions on H₂ co-production. Table 1 summarizes the key scenarios evaluated. Scenario A evaluates different

FIGURE 1. Hydrogen co-production available for vehicles is analyzed as a function of fuel cell stack polarization, cell power density, and cell operating temperature (600°C to 1,000°C).

TABLE 1. Analysis Scenarios for Excess Hydrogen Calculations

Scenario	Parameter Varied	Description	Values
A	Inlet stream temperature	Evaluate performance at the extreme inlet temperatures	1. $T_{inlet-all} = T_{system}$; 2. $T_{inlet-fuel} = T_{ambient}$, 3. $T_{inlet-all} = T_{ambient}$
B	Steam-to-carbon ratio (S/C)	Compare stoichiometric S/C relative to excess steam	S/C = 2 S/C = 4
C	Pure oxygen as oxidant	Baseline case	S/C = 2
D	Air as oxidant	Compare impact of pure air as feed	Air is 78% nitrogen and 22% oxygen by volume
E	Non-ideal cathode utilization	Compare the impact of inefficient oxidant utilization	Utilization of oxygen at the cathode is as low as 25%
F	Biogas fuel	Compare natural gas with a typical biogas feed stream	Biogas is modeled as 65% CH_4 , 32% CO_2 , and 3% H_2O by mole fraction

levels of internal heat transfer within the system on H_2 co-production. Scenario A1 evaluates inlet reactant temperatures at the fuel cell/fuel reformer operating temperature (perfect heat transfer between hot exhaust gases and cold inlet gases.) Scenario A2 evaluates the inlet temperature of the reactant fuel at ambient temperature, and inlet oxidant and water temperature at system temperature. Scenario A3 evaluates conditions in which the inlet temperatures of all reactants are set to ambient temperature (no heat transfer between hot exhaust gases and cold inlet gases.) Scenario B evaluates excess H_2 with respect to a stoichiometric steam-to-carbon ratio (S/C) (equal to two) and to excess steam (S/C = 4). Scenario C evaluates pure oxygen as the oxidant, with a stoichiometric S/C of two, and serves as a base case. Scenario D evaluates air as the oxidant. Scenario E evaluates non-ideal cathode utilizations, with the percentage of oxygen reacting at the cathode as low as 25%. Scenario F evaluates excess H_2 from biogas fuel, derived from waste water treatment plant anaerobic digester gas. Biogas is modeled as being composed of 65% CH_4 , 32% CO_2 , and 3% H_2O by mole fraction. These initial biogas analyses do not consider the upstream energy needed to run the low temperature anaerobic digester, which consumes the majority of available heat from the fuel cell.

C. Develop and apply chemical engineering models for analyses of hydrogen separation and purification sub-systems

In this third of three distinct modeling efforts, we developed detailed chemical engineering process plant models and analyses in Aspen Plus® and conduct scenario analyses using these models to better design one of the most important sub-systems within an H_2 -FCS, the HSU. An HSU PSA unit requires inlet gas at relatively low temperature (323 K) and high pressure (20 bar). Since the anode-off gas of an MCFC is at high temperature (923 K) and low pressure (1.06 bar), a significant energy penalty could be associated with the required compression (146 kWe) and heat extraction (600 kWt)

for a 1 MWe FCS. In addition, currently, in most FCS designs, H_2 that is not consumed in the fuel cell anode compartment is exhausted from the stack in the anode off-gas (exhaust) and combusted in a catalytic afterburner to provide heat for upstream endothermic processes (such as fuel processing and preheating reactants). FCE, Inc. uses this approach in its standard system design. If instead, H_2 is separated prior to the afterburner for co-production, less H_2 and therefore less heat is available from the combustor for heating upstream processes. For a 1 MWe FCS, this lack of available H_2 for combustion can lead to an overall thermal energy deficit of 123 kWt for steam generation and for preheating air and fuel. This is the baseline case HSU design: heat is removed from the anode off-gas to drop the temperature from 923 K down to 323 K without recovering this heat for use in other parts of the system.

By contrast, we analyze alternative HSU designs, and propose new designs, called HSU 1 and HSU 2 (shown in the Figures 2 and 3), as improvements over the baseline case. Both HSU 1 and HSU 2 systems integrate the fuel cell balance of plant with the heat extraction steps required for the PSA. HSU 2 incorporates the same components as HSU 1: heat exchangers, compressors and WGSR. However, these

FIGURE 2. HSU 1 Schematic Diagram

FIGURE 3. HSU 2 Schematic Diagram

system components are arranged in a different order for the two designs. With both configurations, enough heat is recovered to produce all of the high quality inlet steam needed for the FCS operation. Scenario analyses were performed to find appropriate design configurations that reduce the compression work requirements (parasitic loads that reduce gross power output) by reducing compressor inlet temperatures. In addition, scenario analyses were performed to achieve neutral system water balance, such that the overall FCS requires no net addition of liquid water input. Since anode-off gas temperature is dropped below its saturation point, steam condensation takes place in both evaporators. As a result, liquid water can be separated from the gas stream lowering compression work and providing a water supply for the upstream steam reforming process. In HSU 1, a WGSR has been integrated into the system after the compression stage. In HSU 2, the WGSR has been placed before the compressor steps. In both designs, H_2 yield increases by shifting CO and H_2O into H_2 and CO_2 compared to the baseline case. (The HSU baseline configuration is very similar to HSU 1 in terms of component order, but it does not recover the extracted heat to produce steam. Instead of raising steam, heat extracted is not recovered. It also does not include a WGSR.)

Results

A. Develop and apply integrated engineering, economic, and environmental optimization and analysis models

In this first of three distinct modeling efforts, our engineering, economic, and environmental model results show benefits of using H_2 -FCS for electricity, heat and H_2 consumers; FCS manufacturers; and the environment.

Cost Optimization:

For the cases analyzed, our model shows that electricity, heat, and H_2 can be produced with the lowest

costs for strategies that combine these novel features: (1) electrical and thermal networking, (2) variable heat-to-electric power ratio, (3) variable H_2 -to-heat ratio, (4) maximum FCS electrical output, and then (5) H_2 and heat load-following. As long as H_2 -FCS are grid-connected with a competitive electricity sell-back price, they can sell excess electricity not used to the local grid utility network for revenue. By contrast, both heat and H_2 demand are locally constrained, without storage in the current models. Less fuel is wasted when they are produced in load-following mode, yielding higher energy cost savings. The optimal order of H_2 and heat load-following depends upon the relative price of heat compared to H_2 ; as the competing generator price for H_2 rises relative to the heat price, global costs are lower when H_2 -FCS first run in H_2 load-following mode followed by heat load-following mode. As the competing price of heat rises relative to H_2 , it becomes more important for H_2 -FCS to run in heat load-following mode first, and then H_2 load-following.

Figure 4 shows example results for cost optimization for thirteen different strategies evaluated at a competing H_2 generator price of \$4/kg H_2 . At this relatively low H_2 price, the most economical strategy is nine (ix) or NVYEXHP, which stands for electrical and thermal networking [N], variable heat-to-electric power ratio [V], variable H_2 -to-heat ratio [Y], maximum FCS electrical output [EX], and then heat load-following [H], followed by H_2 load-following [P].

CO_2 Optimization:

For the cases analyzed, our model shows that electricity, heat, and H_2 can be produced with the lowest CO_2 emissions for strategies that combine these novel features: (1) electrical and thermal networking, (2) variable heat-to-power ratio, (3) variable H_2 -to-heat ratio, (4) first load-following heat, then load-following H_2 , and finally (5) operating with any of these three modes: electrical load-following, maximum electrical output, and minimum electrical output. With this approach, less fuel is wasted. These results indicate that a primary constraint to minimizing CO_2 emissions is to have the systems load follow heat first (over and above

FIGURE 4. Optimizing For Lowest Energy Costs

electricity). If systems are grid-connected, any electricity not consumed by the local energy area displaces grid electricity. By contrast, heat and H_2 demand are locally constrained without storage, which makes it important to load-follow with these outputs to maximize the amount of useful output per unit of fuel consumed. For the cases evaluated, heat load-following is more crucial than following H_2 demand due to the greater quantity of heat demand compared with H_2 demand in the scenarios investigated.

Figure 5 shows results for CO_2 minimization for thirteen different strategies. The strategies with lowest CO_2 emissions are five, six, and eight, or NVYHPEN, NVYHPE, and NVYHPEX, respectively. All three strategies prioritize electrical and thermal networking [N], a variable heat-to-electric power ratio [V], a variable H_2 -to-heat ratio [Y], and then heat load-following [H], followed by H_2 load-following [P]. The strategies only vary by whether the H_2 -FCS produces the minimum amount of electricity [EN], electrically load follow [E], or produce at their maximum electrical output [EX].

B. Develop and apply thermodynamic and chemical engineering models for analyses of complete FCSs

In this second of three distinct modeling efforts, we analyzed the H_2 co-production potential as a function of various input parameters. Summary results for one case are shown in Figure 6, which applies our simplified analytical model to daily operation. Figure 6 shows the daily H_2 output as a function of SOFC/reformer operating temperature between 600°C and 1,000°C and accounting for all of the cell polarizations (voltage losses) at several operating cell current densities. As shown in Figure 6, a 1 MWe SOFC operating between 800 and 1,000°C could make as much as ~150 to 450 kg of H_2 /day without added fuel consumption or greenhouse gas emissions from fuel combustion for providing heat to the steam reforming reaction.

The quantity of H_2 co-production available is sensitive to several FCS operating conditions. At higher current densities, voltage losses (polarizations)

increase and cell voltage declines. Cell voltage is proportional to the fuel cell stack electrical efficiency. As electrical efficiency declines, the potential for heat recovery increases. With a greater quantity of available heat, more H_2 can be generated. The H_2 co-production per unit of electrical work increases with higher irreversibilities (losses). This trend occurs to a greater extent as temperature decreases, because as the temperature decreases in the range of 600-1,000°C, the polarization increases, especially the ohmic polarization associated with ion conduction through the electrolyte. These results are for operation on oxygen (O_2). While operation on air would reduce the net electrical output of the fuel cell (due to blower parasitic loads,) it would not affect the quantity of H_2 co-produced significantly.

One of the most sensitive variables that affects H_2 co-production potential is the degree of internal heat transfer between hot outlet gases and cold inlet gases. A comparison of Figures 7 and 8 reveals the effects of this variable. Figure 7 shows the quantity of excess H_2 co-produced per unit of methane fuel input as a function of fuel cell/reformer operating temperature for Scenario A1 (100% heat transfer between hot outlet gases and cold inlet ones, with an S/C =2). Figure 8 shows both Scenario A3 (0% heat transfer between hot outlet gases and cold inlet ones, with a S/C =2) and Scenario B (comparison of S/C =2 and 4). The difference between H_2 co-production available in Scenario A1 and Scenario A3 is shown by comparing the solid lines of similar color in each figure. As shown in Figure 8, with no internal heat transfer, operating between 800°C and 1,000°C fuel cell/reformer operating temperature at current densities of 200 mA/cm² and below, no excess fuel cell heat is available and no excess H_2 can be produced. Over the full range of current densities within this temperature range, the H_2 yield is between about 0% and 50% of the H_2 yield with full internal heat transfer.

H_2 co-production potential is greater with more internal reuse of heat between hot outlet and cold inlet gases. Excess H_2 is greater with (A) ideal heat

FIGURE 5. Optimizing for Minimum CO_2 Emissions

FIGURE 6. Excess hydrogen as a function of fuel cell operating temperature and polarization.

transfer between hot FCS exhaust gases (CO_2 , H_2O , H_2) and cold inlet gases (O_2 , CH_4 , H_2O) compared with (B) no heat transfer between hot exhaust and cold inlet streams. The quantity of H_2 co-production increases as the efficiency of heat exchange rises for preheating cold anode and cathode inlet gases with hot anode and cathode exhaust gases. The lower the temperature of inlet streams, the more pre-heating they require, and the less heat is available for H_2 co-production. Figure 8 also shows the impact of operating at a higher S/C. The solid lines represent a S/C of 2 and the dashed lines represent a S/C of 4. More inlet water at ambient temperature requires more pre-heating, and the excess heat available for H_2 declines.

C. Develop and apply chemical engineering models for analyses of hydrogen separation and purification sub-systems

In this third of three distinct modeling efforts, HSU 1 and HSU 2 designs integrate the fuel cell balance of plant with the heat extraction steps required for the PSA. Table 2 summarizes the performance of each design with

FIGURE 7. Excess hydrogen relative to fuel (methane) input for 100% heat transfer between hot and cold streams, S/C = 2.

FIGURE 8. Excess hydrogen relative to fuel input for 0% heat transfer between hot and cold streams, S/C = 2 and 4.

respect to the base case design (no heat recovery). HSU 1 increases the H_2 yield by 132% to 254 kg H_2 /day and HSU 2 increases the yield by 172% to 298 kg H_2 /day, relative to a base case. For a 1 MWe FCS, both HSU 1 and HSU 2 recover 435 kWt of heat from the anode off-gas, or 73% of available heat, to produce high quality steam for the upstream steam reforming reactions. HSU 2 was specially configured so as to reduce compression work requirements by reducing the compressor's inlet gas temperature and the quantity of water vapor in the anode off-gas stream entering the compressors. With the HSU 2 design, the anode-off gas temperature is dropped below its saturation point, such that steam condensation takes place in both evaporators. By condensing the water prior to the compressor, the gas flow and temperature were reduced, reducing the required compression work. Liquid water is separated from the gas stream lowering the compression work and PSA separation requirements. Consequently, HSU 1 compression work requires 114 kW, 11% of gross power, while HSU 2 compression work requires only 71 kW, or 7% of gross power.

TABLE 2. Comparison of the Performance of Different HSU Designs

Molten Carbonate Fuel Cell System (MCFC) (1 MWe)	Base case	HSU 1	HSU 2
H_2 Co-production	Yes	Yes	Yes
Heat Recovery from the Hydrogen Separation Unit (HSU)	No	Yes	Yes
Water-Gas Shift	No	Yes	Yes
Generated Gross Power [kW]	1,000	1,000	1,000
Ancillary loads (compressors) [KW]	114	114	71
Thermal energy penalty to reach PSA levels [kW]	600	600	600
Heat recovered from HSU by steam production [kW]	0	435	435
Heat recovered from HSU by steam production [%]	n.a.	73 %	73 %
Hydrogen potential after WGSR (before PSA) [kmol/s]	0.00151	0.00173	0.00203
Hydrogen produced [kmol/s]	0.00063	0.00147	0.00173
Hydrogen produced [kg/day]	110	254	298
Marginal increase in H_2 compared with base case (kg H_2 /day)	n.a.	144	188
H_2 production increase (Benchmark: NO heat recovery; NO WGS)	n.a.	132%	172%

n.a. - not applicable

HSU 2 also achieves neutral water balance within the entire FCS, having condensed enough water for internal recycle to other parts of the system. In both

designs, the WGSR increases the H_2 yield by shifting CO and H_2O into H_2 and CO_2 . In HSU 2, the WGSR inlet temperature is lowered to increase the H_2 yield. For the HSU 1 design, the individual contributions to the increase in H_2 yield are: 1) 102% due to displaced H_2 combustion; 2) 15% due to WGSR; and 3) 132% due to both.

Conclusions and Future Directions

A. Develop and apply integrated engineering, economic, and environmental optimization and analysis models

- H_2 -FCS operating in novel configurations can be more economical and environmentally benign than state-of-the-art competing generators for electricity, heat and H_2 .
- For the cases evaluated, global CO_2 emissions from H_2 , electricity, and heat are lowest when H_2 -FCS are electrically and thermally networked, use a variable heat-to-power ratio, use a variable H_2 -to-heat ratio, and first load-follow either heat or H_2 demands, depending upon which energy quantity is greater. The electrical output control strategy is a lower priority for CO_2 emissions concerns. This is due primarily to the assumption that excess electricity can be exported to the grid and due to the comparable electrical efficiency of the FCS compared to that of state-of-the-art competing generators.
- Global energy costs for H_2 , electricity, and heat are lowest when H_2 -FCS are networked, use variable heat-to-power ratio, use a variable H_2 -to-heat ratio, and first produce at their maximum electrical output continuously, and then load follow either heat and H_2 demands. High relative prices of heat compared to H_2 shift the optimal control towards heat load-following first and H_2 load-following second, and vice versa.

B. Develop and apply thermodynamic and chemical engineering models for analyses of complete FCSs

- An idealized 1 MW_e fuel cell operating between 800 and 1,000°C could make between ~150 to 450 kg H_2 /day: enough to refuel between 220 and 660 H_2 fuel cell cars per day, without added fuel use or CO_2 emissions from combustion to provide heat for the endothermic steam reforming reaction.
- The quantity of excess H_2 available is very sensitive to the degree of internal heat transfer between cold inlet gases entering the system and hot anode and cathode off-gas streams.
- The quantity of H_2 co-production potential is very sensitive to the inlet temperature of fuel, oxidant, and water streams. Inlet streams at lower

temperature require more preheating, and result in less heat for H_2 co-production.

- For example, an SOFC/reformer operating between 800°C and 1,000°C, and cells operating at 200 mA/cm^2 with no internal heat transfer between hot outlet and cold inlet streams will have no excess fuel cell stack heat available for H_2 co-production without added fuel consumption for combustion. At higher current densities, the H_2 yield is between 0% and about 50% of the H_2 yield with full internal heat transfer.
- With no internal heat transfer, with an SOFC operating between 800°C and 1,000°C at current densities of 200 mA/cm^2 and below, no excess fuel cell stack heat is available and therefore no excess H_2 can be produced.
- To maximize excess H_2 co-production, internal heat transfer to cold streams from hot ones must be maximized and ambient inlet stream temperatures increased through internal heat transfer.
- At higher current densities, voltage losses (polarizations) increase, cell voltage declines, available heat increases, and more H_2 can be co-produced.
- The excess H_2 per unit of electrical work increases with higher irreversibilities. This trend occurs to a greater extent as temperature decreases, because as temperature decreases in the range of 600-1,000°C, the polarizations (mainly ohmic and activation polarization) increase.

C. Develop and apply chemical engineering models for analyses of hydrogen separation and purification sub-systems

- We identified an optimal HSU cycle design that increases H_2 yield by 172%.
- Our proposed design meets PSA unit inlet temperature and pressure requirements, recovers 73% of available anode-off gas heat, consumes only 7% of gross electricity, and increases H_2 yield by 172% to 298 kg H_2 /day (compared with the base case with no heat recovery or WGS). This design also achieves neutral water balance, and minimizes fuel consumption and CO_2 emissions by re-using available heat and minimizing losses.
- One of the most important design conditions for enhancing H_2 yield is internal reuse of available heat.
- For separating out dilute H_2 from hot, low pressure anode off-gas, PSA technology is limited by requirements for: (1) gas delivery at high pressure, (2) low temperature, and (3) with high H_2 concentration; and (4) high ancillary loads for compression that diminish net electric power output. However, PSA technology is commercially available.

- Careful engineering design of the HSU can significantly increase H_2 yield, overall system efficiency, net electric power output, and the system ability to achieve neutral or positive net water balance.

Sandia plans to pursue further research in these areas:

- Enhance and integrate chemical engineering FCS and sub-system models.
- Enhance economic and environmental network models.
- Expand further chemical engineering FCS and sub-system models.
- Expand further economic and environmental network models.
- Integrate chemical engineering and economic and environmental models.
- Analyze case studies for controlling and operating advanced poly-generative fuel cell systems (PFCS).
- Independently verify PFCS costs based on industry best practice methods.
- Integrate PFCS models with models of advanced renewables and energy storage.
- Collaborate with other national labs on model development and integration.

Special Recognitions & Awards/Patents Issued

- American Society of Mechanical Engineers (ASME) Keynote Speaker Award* for presenting this keynote paper: Whitney Colella, Arel Rankin, Amy Sun, Pere Margalef, Jack Brouwer, "Engineering Design and Control of Polygenerative Fuel Cells," *ASME 7th International Fuel Cell Science, Engineering, and Technology Conference*, Newport Beach, CA, USA, June 8–10th, 2009.

FY 2009 Publications/Presentations

Oral Presentations

- Colella, W.G., Rankin, A., Margalef, P., Brouwer, J., Sun, A., "Releasing Low, Zero, or Negative Net Carbon Dioxide Emissions by Polygenerating Electricity, Recoverable Heat, Cooling Power, and Hydrogen Fuel with Novel Fuel Cell Designs," *2nd Annual Earth, Wind, and Sun Conference*, Sandia National Laboratories, Albuquerque, NM, July 22nd, 2009.
- Whitney Colella, Arel Rankin, Pere Margalef, Jack Brouwer, Amy Sun, "Polygenerating Electricity, Recoverable Heat, Cooling Power, and Hydrogen Fuel with Fuel Cell Systems," *Energy Seminar at the Solar Thermal Power Tower*, Sandia National Laboratories, Albuquerque, NM, USA, July 13th, 2009.
- Whitney Colella, "Implementing Stationary Fuel Cell Systems in Novel Ways to Poly-generate Electricity,

Recoverable Heat, Cooling Power, and Hydrogen Fuel Based on Thermodynamic, Economic, and Environmental Models," *Energy Systems Analysis Department Colloquia*, Sandia National Laboratories, Albuquerque, NM, USA, July 13th, 2009.

- Pere Margalef, "Hydrogen Generation with High-Temperature Fuel Cells," *Advanced Power and Energy Program Seminar Series*, University of California, Irvine, Irvine, California, June 26th, 2009.
- Whitney Colella, Arel Rankin, Melahn Parker, "Economic and Environmental Optimization Models for Refining Fuel Cell Use," *32nd International Association of Energy Economics (IAEE) International Conference -- Energy, Economy, Environment: The Global View*, San Francisco, CA, June 21st–24th, 2009.
- Whitney Colella, Arel Rankin, Amy Sun, Pere Margalef, Jack Brouwer, "Designing Next-Generation Fuel Cells for Poly-generating Electricity, Recoverable Heat, Cooling Power, and Transportation Fuels," *Electric Power Conference*, Rosemont, Illinois, May 12th, 2009.
- Whitney Colella, "Innovative Fuel Cells for Poly-generating Electricity, Heat, and Transportation fuels," *ENG300 Energy Systems Course Seminar*, Sandia National Laboratories, Albuquerque, NM, USA, May 5th, 2009.
- Whitney Colella, Arel Rankin, Amy Sun, Melahn Parker, Jack Brouwer, Pere Margalef, "Optimal Design, Installation, and Control Strategies for Cogenerative Distributed Fuel Cells," *École Polytechnique Fédérale de Lausanne (EPFL) Seminar*, Laboratoire d'énergétique industrielle, Lausanne, Switzerland, April 2nd, 2009.
- Whitney Colella, Arel Rankin, Amy Sun, Melahn Parker, Jack Brouwer, Pere Margalef, "Advanced Low Carbon Distributed Generation," *E4Tech Seminar*, Lausanne, Switzerland, April 1st, 2009.
- Whitney Colella, Amy Sun, Jack Brouwer, Pere Margalef, "Advanced Strategies for Stationary Fuel Cell Systems (FCS)," *International Energy Agency (IEA) Advanced Fuel Cells Annex: Stationary applications Annex XIX Meeting*, Vienna and Güssing, Austria, March 25th–26th, 2009.
- Whitney Colella, Arel Rankin, Amy Sun, Melahn Parker, Jack Brouwer, Pere Margalef, "Advanced Cogenerative and Polygenerative Fuel Cell System Design," *Fraunhofer Institute for Solar Energy (ISE) Systems Seminar*, Freiburg, Germany, March 31st, 2009.
- Whitney Colella, Arel Rankin, Amy Sun, Jack Brouwer, Pere Margalef, "Dynamic System Modeling of Integrated Fuel Cell Systems with Hydrogen Co-Production," *Fuels Pathways Integration Technology Team (FPITT) Meeting*, National Renewable Energy Laboratory (NREL) offices, Washington, D.C. (remotely delivered), March 17th 2009.
- Pere Margalef, Jack Brouwer, Scott Samuelson, "Tri-Generation of Electricity, Hydrogen, and Heat on Demand from High-Temperature Fuel Cells," *International Colloquium on Environmentally Preferred Advanced Power Generation (ICEPAG)*, Newport Beach, California, Feb. 10th–12th, 2009.

Poster Presentations

1. Whitney Colella, Arel Rankin, Amy Sun, Pere Margalef, Jack Brouwer, "Thermodynamic, Economic, and Environmental Modeling of Hydrogen (H₂) Co-Production Integrated with Stationary Fuel Cell Systems (FCS)," 2009 U.S. Department of Energy Hydrogen Program Annual Merit Review & Peer Evaluation Meeting, Arlington, VA, May 18–22nd, 2009.

Reports

1. Whitney Colella, Arel Rankin, Pere Margalef, Amy Sun, Jack Brouwer, "Thermodynamic, Economic, and Environmental Modeling of Hydrogen (H₂) Co-Production Integrated with Stationary Fuel Cell Systems (FCS), 2009 U.S. Department of Energy Hydrogen Program Annual Report, Albuquerque, NM, July 1st, 2009.

VII.18 Stranded Biogas Decision Tool for Fuel Cell Co-Production

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Project Start Date: June 1, 2009
Project End Date: September 30, 2011

- (C) Inconsistent Data, Assumptions and Guidelines
- (D) Suite of Models and Tools

Contribution to Achievement of DOE Systems Analysis Milestones

This project contributes to the achievement of the following DOE milestones from the Systems Analysis section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- **Milestone 5:** Complete analysis and studies of resource/feedstock, production/delivery and existing infrastructure for various hydrogen scenarios. (4Q, 2009)

Objectives

- Use geographic information system (GIS) analysis of clustered stranded biogas sites; overlay transportation and transmission infrastructure information and assess the geo-spatial conditions conducive to creating a renewable fuel cell supply chain based on biomethane.
- Identify supply chain scenarios that minimize the global warming potential of emissions, optimize the capture and use of methane from geographically dispersed sources, and minimize water consumption.
- Analyze supply chain scenarios for the capture and use of methane from geographically dispersed sources with respect to potential reduction of global warming emissions and water consumption.
- Identify applicable federal and state tax-based incentives, tariffs, and grants that capitalize on the diverse set of financing opportunities associated with multiple sources of biogas and biomethane production pathways, and combined heat and power and energy conversion technologies.
- Develop and test decision-making tools based on regional biomethane supply chain scenarios and appropriate financing opportunities.

Technical Barriers

This project addresses the following technical barriers from the Systems Analysis section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) Future Market Behavior

Approach

NREL will identify data and literature resources for technical and cost information related to the equipment and processes needed to utilize stranded biogas resources as well as spatial data on sources of biogas including volume and composition. We will also gather real-world usage, reliability, and cost data on biogas-fuel cell installations, making sure to cover a variety of biogas sources, with different clean-up requirements and types of fuel cells. We will then use NREL's extensive GIS capabilities, focusing initially on California, to map stranded biogas resources and overlay infrastructure information, such as highways, pipelines, cost of electricity and natural gas, and energy usage. This will enable us to perform analyses on resources and infrastructure that will assist with the development of deployment scenarios. We will also work with energy financing and tax law experts to identify applicable federal and state grant, tax incentives, and loan/debt instruments and outline the impact each of these instruments will have against each of the proposed scenario cost structures.

This work will lead to an analysis workshop attended by stakeholders in state and federal governments, utilities, equipment suppliers, and site developers, as well as energy end-users. This workshop will address a range of issues related to biogas fuel cell systems. NREL will present results of GIS mapping data and analysis of selected scenario examples, the influence of federal and state financial incentives on different biogas project structures, and overviews of biogas producing facilities that include experiences with digestion, clean-up, use of biomethane, and potential water issues. The workshop will explore the feasibility

and utility of using stranded biogas resources in fuel cell co-production networks as well as lay the basis for development of analysis and decision-making tools for potential biogas sources and energy end-users to evaluate the economic feasibility of deploying these systems.

Accomplishments

- Identified and communicated with California stakeholders in state and federal governments; utilities, industry and academic groups; and fuel cell suppliers.
- Identified several potential fuel cell supply chain scenarios for efficient and cost-effective biogas production and biomethane cleanup and delivery to a stationary fuel cell.
- Identified and began initial data gathering of stranded biogas resource sites in California.

FY 2009 Publications/Presentations

1. DOE Hydrogen Program Annual Merit Review, poster presentation, May 2009.

VIII. TECHNOLOGY VALIDATION

VIII.0 Technology Validation Sub-Program Overview

Introduction

The Technology Validation Sub-Program has been focused on conducting learning demonstrations that emphasize co-development and integration of hydrogen infrastructure with hydrogen fuel cell-powered vehicles to permit industry to assess progress towards technology readiness. Technology Validation tests, demonstrates and validates hydrogen fuel cell vehicles and infrastructure and uses the results to provide feedback to the Hydrogen R&D Program.

Goal

Validate the status of meeting Program targets for integrated hydrogen and fuel cell technologies for transportation, infrastructure and electric generation under real-world operating conditions for both the transition and mature market periods.

Objectives

- By 2008, validate that hydrogen vehicles have greater than 250-mile range without impacting passenger or cargo compartments.
- By 2009, validate 2,000-hour fuel cell durability in vehicles and hydrogen infrastructure that results in a hydrogen production cost of less than \$3.00/gasoline gallon equivalent (gge) (untaxed and dispensed) and allows for safe and convenient refueling by drivers (with training).
- By 2014, validate \$1.60/gge (at the plant gate) hydrogen cost from biomass gasification and \$3.10/gge for central wind-based electrolysis at the plant gate.
- By 2015, validate hydrogen vehicles that have greater than 300-mile range, 5,000-hour fuel cell durability, and hydrogen infrastructure that results in a hydrogen production cost of \$2.50/gge (untaxed) and allows for safe and convenient refueling by drivers (with training).

Fiscal Year 2009 Technology Status

In 2009, the National Learning Demonstration continued to provide data for evaluating the technology status with respect to fuel cell durability, driving range, and power park demonstrations. Data collected during the past four years has been analyzed. Thus far, more than 1.9 million miles have been traveled by the fuel cell vehicles in the project, and 90,000 kg of hydrogen either produced or dispensed. The fuel cell durability has reached nearly 2,000 hours, and the vehicle range has exceeded the goal of 250 miles. Fuel cell system efficiency data at ~25% net power is 53–58% which is close to the DOE target of 60%.

High-pressure gas storage is approaching adequate refueling times and rates for consumers. Twenty-four percent of the vehicles have experienced flow rates >1 kg/m (DOE's near-term target).

FY 2009 Accomplishments

National Learning Demonstration

- Generation 1 and 2 vehicles continued to be operated by customers, hydrogen refueling stations were installed and operated, and data were provided to the Hydrogen Secure Data Center at the National Renewable Energy Laboratory.
- All Generation 2 vehicles have been placed into service, bringing the total number of Generation 1 and 2 vehicles in the project to 140.
- A total of 20 hydrogen fueling stations are currently in operation, located in Northern and Southern California; Orlando, FL; Washington D.C.; Detroit, MI; and the New York City area.

Learning Demonstration Project Teams and Their Two Generations of Vehicles¹

Hawaii Hydrogen Power Parks

- Issued a Request for Proposal for the “turn-key” supply of the hydrogen production/fueling system - selection to be completed by September 30, 2009.
- Worked with the Hawaii Volcanoes National Park and the Hawaii Center for Advanced Transportation Technologies to develop a specification for the shuttle buses, and obtained quotes from suppliers.

Energy Station at Fountain Valley²

- Air Products and FuelCell Energy completed the initial phase of validation testing of the Hydrogen Energy Station at FuelCell Energy’s facilities in Danbury, CT. The system has operated at up to 50% load, and has met expectations for hydrogen production, purity and recovery, and for net power production.
- Air Products executed an agreement with the California Air Resources Board (CARB) to support the existing DOE program and to add a new 100 kilogram per day fueling station to provide

¹ U.S. Fuel Cell Vehicle Learning Demonstration: Status Update and Early Second-Generation Vehicle Results, Keith Wipke et al, National Renewable Energy Laboratory, EVS24, Stavanger, Norway, May 13-16, 2009.

² Hydrogen Energy Station is a technology that co-produces power, heat and hydrogen. This type of system is often referred to as CHHP (Combined Heat, Power and Hydrogen). As shown in the figure, the station uses a high-temperature fuel cell to co-generate electricity, heat and hydrogen. The fuel cell can use a diversity of hydrogen-rich fuels, including digester gas, natural gas, landfill gas and syngas. This technology is expected to provide a source of cost-competitive, renewable hydrogen.

Energy Station Concept for Fountain Valley

renewable hydrogen to fuel cell vehicles. The system will be installed and operated for three years under the CARB program at Orange County Sanitation District in Fountain Valley, CA. The board of the South Coast Air Quality Management District has also approved funding for the project.

Budget

The funding portfolio for Technology Validation addresses the need to validate integrated hydrogen and fuel cell technologies for transportation, infrastructure, and electric generation in a systems context under real-world operating conditions. The FY 2009 funding was appropriated under the Vehicle Technologies Office in the Hybrid Electric Systems Activity.

The President's FY 2010 budget request realigns the Hydrogen Program to focus on nearer term impacts to our Nation's most pressing energy needs. Therefore, funding was not requested for the Technology Validation Activity in FY 2010.

FY 2010 Plans

In FY 2010 all of the National Learning Demonstration projects will be concluded and final reports will be prepared.

The program's validation activities also encompass fuel cell buses (FCBs). Collaboration with the Department of Transportation includes validating fuel cell and hydrogen technologies in transit bus applications in coordination with the Federal Transit Administration, and harmonizing data collection efforts with other FCB demonstrations worldwide.

Under our Market Transformation program element, DOE has collaborated with the Defense Logistics Agency (DLA) on the demonstration of fuel cell forklifts. As the main provider of fuel and supplies for the Department of Defense as well as several civilian agencies, DLA supports a vast infrastructure of distribution centers across both the United States and abroad. By introducing fuel cell forklifts into their distribution centers, DLA capitalizes on an excellent opportunity for testing fuel cells under real world conditions, and providing feedback to manufacturers. As part of this effort, NREL will collect and analyze the operations and performance data of the fork lifts.

As the program develops a more diverse portfolio of projects that include early market applications, the Technology Validation effort will be expanded to collect and analyze data from stationary fuel cells.

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VIII.1 Controlled Hydrogen Fleet and Infrastructure Analysis

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Start Date: October 2003

Projected End Date: September 2010

Objectives

- By 2008, validate that hydrogen vehicles have greater than a 250-mile range without impacting passenger or cargo compartments.
- By 2009, validate 2,000-hour fuel cell durability in vehicles and hydrogen infrastructure that results in a hydrogen production cost of less than \$3.00/gasoline gallon equivalent (gge) (untaxed) delivered, and safe and convenient refueling by drivers (with training).
- Assist DOE in demonstrating the use of fuel cell vehicles (FCVs) and hydrogen infrastructure under real-world conditions, using multiple sites, varying climates, and a variety of sources for hydrogen.
- Analyze detailed fuel cell and hydrogen data from vehicles and infrastructure to obtain maximum value for DOE and industry from this "learning demonstration."
- Identify the current status of the technology and its evolution over the project duration; generate composite data products (CDPs) for public dissemination.
- Provide feedback and recommendations to DOE to assist hydrogen and fuel cell research and development (R&D) activities and assess progress toward technology readiness.

Technical Barriers

This project addresses the following technical barriers from the Technology Validation section (3.6.4) of the Hydrogen, Fuel Cells and Infrastructure Technologies (HFCIT) Program Multi-Year Research, Development, and Demonstration Plan:

- (A) Lack of Fuel Cell Vehicle Performance and Durability Data
- (B) Hydrogen Storage
- (C) Lack of Hydrogen Refueling Infrastructure Performance and Availability Data
- (D) Maintenance and Training Facilities
- (E) Codes and Standards
- (H) Hydrogen from Renewable Resources
- (I) Hydrogen and Electricity Co-Production

Contribution to Achievement of DOE Technology Validation Milestones

Over a five-year period, researchers in this project are gathering data and providing technical analysis that is contributing to achieving the following DOE technology validation milestones from the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development, and Demonstration Plan (MYRDDP):

- **Milestone 2: Demonstrate FCVs that achieve 50% higher fuel economy than gasoline vehicles (Q3, FY 2005).** Vehicle chassis dynamometer testing was completed on 11 vehicles to obtain accurate fuel economy data from the four industry teams. While some of the Learning Demonstration vehicles are not sold in the United States, and therefore don't have a benchmark U.S. fuel economy to compare to, data show that the fuel economy of the FCVs was >50% higher than the equivalent conventional gasoline vehicles. This milestone has been achieved.
- **Milestone 3: Decision for purchase of additional vehicles based on projected vehicle performance and durability, and hydrogen cost criteria (Q4, FY 2006).** At the end of Fiscal Year 2006, NREL used all available fuel cell data to analyze performance against DOE 2006 targets. Based on high fuel cell system efficiency results, good refueling times, and fuel cell voltage degradation that straddled DOE's 1,000-hour target, we recommended that DOE proceed with purchasing 2nd generation FCVs to validate the 2009 targets. This milestone has been achieved.
- **Milestone 4: Operate fuel cell vehicle fleets to determine if 1,000 hour fuel cell durability, using fuel cell degradation data, was achieved by industry (Q4, FY 2006).** In September 2006, NREL analyzed the fuel cell data to date and made projections about fuel cell durability to a 10% voltage degradation. These results were then compared to the 1,000-hour target and formed the basis for a public CDP. At the time of the milestone,

the highest projected team average was 950 hours with a four-team average of just over 700 hours. After two and a half years of additional on-road data (through December 2008), the latest results show the highest projected team average of 1,977 hours with the four-team average of 828 hours. This milestone has been achieved.

- **Milestone 5: Validate vehicle refueling time of 5 minutes or less for a 5 kg tank [1kg/min] (Q4, FY 2006).** NREL used all available project refueling data to compare the refueling rate to the DOE target of 5 kg in five minutes (1 kg/min). At the time of the milestone, we analyzed over 2,000 vehicle refueling events and calculated an average rate of 0.69 kg/min and median rate of 0.72 kg/min, with 18% of the events exceeding the 1 kg/min target. Updates 2.5 years later using over 16,000 refueling events showed improved results with an average rate of 0.78 kg/min with 24% of refueling events exceeding 1 kg/min. This milestone has been achieved.
- **Milestone 7: Validate refueling time of 5 minutes or less for 5 kg of hydrogen (1 kg/min) at 5,000 psi through the use of advanced communication technology (Q4, FY 2007).** While similar to Milestone 5, this milestone specifically addresses communication fills. At the time of the milestone, we calculated an average rate of 0.76 kg/min based on all refueling events, with 23% of the events exceeding the 1 kg/min target. As mentioned in Milestone 5 above, refueling rates have continued to improve since then. We also analyzed the difference in refueling rates of communication and non-communication fills; the data show that communication fills can refuel at a higher rate (up to 1.8 kg/min) and have an average fill rate 35% higher than non-communication fills (0.88 kg/min vs. 0.65 kg/min). This milestone has been achieved.
- **Milestone 8: Fuel cell vehicles demonstrate the ability to achieve 250-mile range without impacting passenger cargo compartment (Q4, FY 2008).** We analyzed the driving range of second-generation FCVs utilizing 700 bar high-pressure hydrogen tanks and compared it to DOE's 2008 target of 250 miles using the window-sticker results which are more realistic than the raw dynamometer test results. The Learning Demonstration results indicate that hydrogen stored on-board vehicles at 700 bar can significantly increase driving range (to between 196–254 miles), however in some cases it still does so at the expense of passenger or cargo volume. In June 2009, an on-road driving range evaluation was performed in collaboration with Toyota and Savannah River National Laboratory, with the results indicating a 431 mile on-road range was possible in southern California from their FCV. No cargo or passenger space was compromised in

that vehicle, but they did give up the spare tire in the packaging of the hydrogen tanks under the rear floor. This milestone has been achieved.

- **Milestone 10: Validate FCVs 2,000 hour fuel cell durability, using fuel cell degradation data (Q4, FY 2009).** On-road fuel cell voltage data from 2nd generation fuel cell systems will be analyzed in a manner similar to the 2006 analysis (including any improvements to the methodology) to evaluate durability and compare it to the 2,000-hour target for the Fall 2009 CDP results.
- **Milestone 11: Decision to proceed with Phase 2 of the Learning Demonstration (Q2, FY 2010).** Based on the progress made between first- and second-generation FCV technologies, NREL will support DOE in the decision to proceed with Phase 2 of the Learning Demonstration.
- **Milestone 23: Total of 10 stations constructed with advanced sensor systems and operating procedures (Q1, FY 2008).** This milestone has been achieved.
- **Milestone 24: Validate a hydrogen cost of \$3.00/gge (based on volume production) (Q4, FY 2009).** We will estimate hydrogen costs at volume using the hydrogen analysis (H2A) tool with support from industry. The results will be included in the Fall 2009 CDPs.

Accomplishments

- Received and processed data from a total of 395,000 individual vehicle trips, amounting to over 88 gigabyte (GB) of on-road data, since inception of the project.
- Created and published 60 CDPs (the seventh such set of public results) representing results from analyzing almost four years of Learning Demonstration data.
- Completed implementation for producing detailed data results and CDPs at the same time for easier industry and internal review.
- Documented and archived each quarter's analysis results in the Fleet Analysis Toolkit (FAT) graphical user interface.
- Presented project results publicly at EVS-24, the Fuel Cell Seminar, the National Hydrogen Association conference, and the 2009 DOE Hydrogen Program Merit Review meeting.
- Kept NREL's Web page up-to-date at http://www.nrel.gov/hydrogen/cdp_topic.html to allow direct public access to the latest CDPs organized by topic, date, and CDP number. This also allowed the results to be indexed directly by Web search engines.
- Made major improvements to NREL's FAT, the tool that automatically processes and analyzes every

vehicle trip file and refueling event and presents the results graphically in an interactive manner.

- Further developed a collaborative technical relationship with all four industry teams by giving presentations to each team, including detailed results on every stack in their fleet.
- Provided presentations of results to key stakeholders, including two FreedomCAR and Fuel technical teams (storage and fuel cells), the US Fuel Cell Council Transportation Working Group, the Joint Hydrogen Quality Working Group, and both the Vehicle Technologies Program and the HFCIT Program.

Introduction

The primary goal of this project is to validate vehicle/infrastructure systems using hydrogen as a transportation fuel for light-duty vehicles. This means validating the use of FCVs and hydrogen refueling infrastructure under real-world conditions using multiple sites, varying climates, and a variety of sources for hydrogen (see Figure 1 for photographs representing the four types of hydrogen refueling stations). Specifically, in 2009 we are validating hydrogen vehicles with greater than 250-mile range, 2,000-hour fuel cell durability, and \$3/gge hydrogen production cost (based on modeling for volume production). We are identifying the current status of the technology and tracking its evolution over

the five-year project duration, particularly between the first- and second-generation FCVs. NREL's role in this project is to provide maximum value for DOE and industry from the data produced by this "learning demonstration." We seek to understand the progress toward the technical targets, and provide information to help move the HFCIT R&D activities more quickly toward cost-effective, reliable hydrogen FCVs and supporting refueling infrastructure.

Approach

Our approach to accomplishing the project's objectives is structured around a highly collaborative relationship with each of the four industry teams, including Chevron/Hyundai-Kia, Chrysler/BP, Ford/BP, and GM/Shell. We are receiving raw technical data from both the hydrogen vehicles and refueling infrastructure that allows us to perform unique and valuable analyses across all four teams. Our primary objectives are to feed the current technical challenges and opportunities back into the DOE Hydrogen R&D Program and assess the current status and progress toward targets.

To protect the commercial value of these data for each company, we established the Hydrogen Secure Data Center (HSDC) to house the data and perform our analysis. To ensure value is fed back to the hydrogen community, we publish CDPs twice a year at technical conferences to report on the progress of the technology and the project, focusing on the

FIGURE 1. Four Types of Hydrogen Refueling Stations are being Tested

most significant results. Figure 2 shows the periodic publication of CDP sets relative to the inflow of vehicle data to NREL. Additional CDPs are being conceived as additional trends and results of interest are identified, and as we receive requests from DOE, industry, and codes and standards committees. We also provide our detailed analytical results (not public) on each individual company's data back to them to maximize the industry benefit of NREL's analysis work and obtain feedback on our methodologies.

Results

The results in FY 2009 came from analyzing an additional year of data (January – December 2008), creating a total of 60 new or updated CDPs, and presenting these results at five technical conferences. To accomplish this, we continued to improve and revise our in-house analysis tool, FAT. Since there are now so many technical results from the project, they cannot all be listed here or be fully presented during brief conference presentations. Therefore, in 2007 NREL launched a new Web page at http://www.nrel.gov/hydrogen/cdp_topic.html to provide the public with direct access to the results. Portions of these results have also been presented publicly at the Fuel Cell Seminar (10/08), the Electrochemical Society conference (10/08), the 2009 National Hydrogen Association meeting (3/09), the EVS-24 conference (04/09), and the Society of Automotive Engineers (SAE) Congress (04/09) as two distinct sets of results (labeled “Fall 2008” and “Spring 2009”). Since all 60 of the results are available now on the Web site, this report will just include some of the highlights over the last year.

- **Vehicle Fuel Economy:** Vehicle fuel economy was measured using city and highway drive-cycle tests on a chassis dynamometer using draft SAE J2572. These raw test results were then adjusted

FIGURE 2. CDPs are Published at Six-Month Intervals

according to U.S. Environmental Protection Agency (EPA) methods to create the “window-sticker” fuel economy that consumers see when purchasing the vehicles (0.78 x Hwy, 0.9 x City). Generation 1 vehicles had an adjusted fuel-economy range of 42 to 57 miles/kg hydrogen for the four teams, and generation 2 vehicles showed a slight improvement in fuel economy to 43 to 58 miles/kg.

- **Vehicle Driving Range:** Vehicle driving range was calculated using the fuel economy results discussed above and multiplying them by the usable hydrogen stored onboard each vehicle. New for this year was the comparison between the two generations of vehicles. Generation 1 vehicles had a range from just over 100 miles up to 190 miles from the four teams, whereas generation 2 vehicles using 700 bar pressure hydrogen tanks showed a significantly improved window-sticker driving range of 196 to 254 miles (Figure 3). This demonstrated that DOE's September 2008 MYRDDP Milestone 8 target of 250 miles was achieved. Note that all of the Learning Demonstration vehicles are based on existing platforms, and higher driving ranges are expected when the vehicles are designed around hydrogen.
- **Fuel Cell Efficiency:** The baseline fuel cell system efficiency was measured from selected vehicles on a vehicle chassis dynamometer at several steady-state points of operation. DOE's technical target for net system efficiency at $\frac{1}{4}$ -power is 60%. Data from the four Learning Demonstration teams showed a range of net system efficiencies from 52.5% to 58.1%, which is very close to the target. These results have not changed since they were first published because they are baseline results for first-generation vehicles, but the teams have tested second-generation systems and these will be evaluated for any efficiency

FIGURE 3. Driving Range for Gen 1 and Gen 2 Vehicles, based on Fuel Economy and Usable H₂

changes as the systems get closer to technology readiness. We anticipate including the range of efficiency curves (idle to full power) in the Fall 2009 results, in addition to just the ¼ power point described here.

- Fuel Cell System Specific Power and Power Density:** Data were received on the total fuel cell system mass, volume, and power. Both the specific power (W/kg) and the power density (W/L) were evaluated for generation 1 and compared with generation 2 fuel cell systems. We found that while the fuel cell system power density stayed about the same between the two generations (ranging from 300 to 400 W/L) there were significant improvements in fuel cell system specific power, improving from generation 1 results of 200–300 W/kg up to generation 2 results of 300–400 W/kg. It appears as though it may take another generation or two before the fuel cell systems achieve DOE's 2010 and 2015 MYRDDP target of 650 W/kg. For the Fall 2009 results we will add a new CDP that includes hydrogen storage as part of the system to allow comparisons with other energy and power systems such as batteries.

- Fuel Cell Durability:** Fuel cell stacks will need roughly a 5,000 hour life to enter the market for light-duty vehicles. Preliminary durability estimates were first published in the fall of 2006 because most stacks at that time only had a few hundred hours of operation or less accumulated on-road. NREL developed a methodology for projecting the gradual degradation of the voltage based on the data received to date. This involved creating periodic fuel cell polarization curve fits from the on-road stack voltage and current data, and calculating the voltage under high current. This enabled us to track the gradual degradation of the stacks with time and do a linear fit through each team's data. We then compared these results to the first-generation target of 1,000 hours for 2006.

In the past two and a half years, many more hours have been accumulated on the fuel cell stacks, and the range of fleet averages is now ~200 to 850 hours, with the range of fleet maximums spanning ~300 to 1,987 hours (Figure 4). This is the first time, to our knowledge, that a light-duty passenger fuel cell car has accumulated almost 2,000 hours in real-world operation without repair to the fuel cell stack, which is a significant project accomplishment. The amount of data extrapolation we have to make using the slope of the linear voltage degradation method (10% voltage drop target divided by the mV/hour slope) continues to decrease as we receive additional data. However, with the additional data we have also found that the accuracy of the 10% voltage degradation projection could be improved by using a non-linear fit to account for the more

FIGURE 4. Gen 1 Stack Operating Hours and Projected Time to 10% Voltage Drop

rapid degradation that occurs within the first few hundred hours. Fuel cell stack degradation results for this project in the Fall 2008 began using a two-segment linear fit and also used a weighting algorithm to come up with a more robust fleet average. The projected times to 10% fuel cell stack voltage degradation from the four teams using this new technique had an average of 828 hours. Note that the 10% criterion, which is used for assessing progress toward DOE targets, may differ from the vehicle manufacturer's end-of-life criterion and does not address "catastrophic" failures such as membrane failure. The second-generation stacks introduced in this project beginning in late 2007 will be compared to the 2,000-hour target in September 2009, and we will also add additional CDPs relating to acceptable power degradation and stack longevity.

- Factors Affecting Fuel Cell Durability:** We continued investigating factors that are affecting the rates of fuel cell stack degradation. Two of these factors that our industry partners asked us to examine were the amount of time the fuel cell spends at various voltage levels and the average number of trips per operating hour. We found that about 15% of the time was spent at roughly the open-circuit voltage and very low current, while only 17% of the time was spent at <70% of the maximum voltage (corresponding to high load). In looking at the average number of trips per hour (Figure 5), we found a normal distribution around the median of roughly four trips per hour. This information was also provided to a fuel cell durability task force that was formulating durability test protocols, as they wanted to make sure they knew what the actual average trips per operating hour was from real stacks in everyday use. We also examined whether there was a trend of average trips

FIGURE 5. Fuel Cell Stack Trips per Hour Histogram

per hour as a function of stack operating hours, and we found that the stacks that have demonstrated long hours (to date) show lower average trips per hour. We will have to accumulate more data before we can attribute a causal relationship between the two.

- Vehicle Maintenance:** Over the four years of vehicle operation, there has been a large set of data collected on all of the vehicle maintenance events. There were a total of 9,357 maintenance events consuming 10,216 hours. We found that 34% of the vehicle maintenance events were due to the fuel cell system, consuming 49% of the maintenance labor. Over half (57%) of the vehicle maintenance events were non-powertrain related. Breaking down the details of the fuel cell system into all of its parts, we found a surprising result: only 11% of the fuel cell system events were due to the fuel cell stack, while the most frequently serviced parts of the fuel cell system were the thermal management system (36%), the air system (26%), controls/electronics/sensors (14%), the fuel system (11%), and then the fuel cell stack (5th down the list). This indicates that the other components in the fuel cell system beside the fuel cell stack itself need more attention and potentially R&D before these vehicles reach the point of commercialization.
- Infrastructure Maintenance:** Like vehicle maintenance, the hydrogen fueling station maintenance data were also analyzed. There were a total of 1,860 infrastructure maintenance events, requiring 9,093 hours. While we assumed that one of the production components would top the list, it was actually the system control and safety systems that accounted for the most maintenance events

(22%) and labor (22%). The four major components of the system including the compressor, electrolyzer, reformer, and dispenser were roughly equal in terms of their maintenance requirements. The hydrogen storage system required the least maintenance at just a couple percent.

- Vehicle Refueling Rates:** Over 16,000 refueling events have been analyzed to date, and the refueling amount, time, and rate have been quantified. The average time to refuel was 3.30 minutes with 87% of the refueling events taking less than five minutes. The average amount per fill was 2.18 kg, reflecting both the limited storage capacity of these vehicles (~4 kg max) and peoples' comfort level with letting the fuel gauge get close to empty. DOE's target refueling rate is 1 kg/minute, and these Learning Demonstration results indicate an average of 0.78 kg/min, with 24% of the refueling events exceeding 1 kg/minute.
- Fueling Rate Comparison Between 350 and 700 bar Fills:** The previously discussed refueling rates included all types of refueling events. There has been much interest from industry and from the codes and standards community on the effect of communication vs. non-communication and 350 bar vs. 700 bar pressure on fill rates. A communication fill means that the vehicle communicates data about the state of its hydrogen storage tank(s), such as tank temperature, pressure, and max pressure rating, to the refueling station. We previously showed that communication fills are capable of having higher average fill rates (0.88 kg/min) than non-communication fills (0.65 kg/min). This year, we also examined the difference in fill rates based on fill pressure (Figure 6), and found that 700 bar fills were currently 27% slower than 350 bar fills. The average 350 bar fill rate was 0.81 kg/min while the average 700 bar fill rate was only 0.59 kg/min.
- On-Site Production Efficiency from Natural Gas Reformation and Electrolysis:** Detailed data on all of the energy inputs required to produce hydrogen on-site were gathered and analyzed and compared to DOE's program targets for 2010 for natural gas reformation and 2012 for water electrolysis. The results indicate that natural gas reformation efficiency was demonstrated close to the 2010 target of 72% through achieving a best quarterly efficiency of 67.1% and a best monthly efficiency of 69.8%. The best quarterly efficiency for water electrolysis was 57.4% with a best monthly efficiency of 60.3% (compared to the 2012 target of 69%). Note that targets for both of these technologies are for future years (2010 and 2012) and results from 2005-2008 were not yet expected to have achieved future targets. Additionally, the targets are set for significantly larger stations (1,500 kg/day of hydroge) and higher utilization

FIGURE 6. Comparison of Fueling Rates for 350 and 700 bar Pressure Fueling Events

(70% capacity factor) than we have in the Learning Demonstration. The purpose of comparing our actual results to these future targets is to benchmark demonstrated progress toward the targets while technical R&D development continues to improve the state-of-the-art.

- Vehicle Greenhouse Gas Emissions (GHGs):** GHGs from the Learning Demonstration fleet have been assessed and compared to greenhouse gas emission estimates of conventional gasoline vehicles. The results indicate that when using hydrogen produced on-site via either natural gas reformation or water electrolysis, Learning Demonstration hydrogen FCVs offer significant reductions of GHGs relative to conventional gasoline vehicles (Figure 7). Conventional gasoline mid-sized passenger vehicles emit 484 g CO₂-eq/mile (grams CO₂-equivalent per mile) on a well-to-wheels (WTW) basis and conventional mid-size sport utility vehicles (SUVs) emit 612 g CO₂-eq/mile on a WTW basis. WTW GHGs for the Learning Demonstration FCV fleet (which includes both passenger cars and SUVs) were analyzed based on the window sticker fuel economy of the Learning Demonstration fleet and the actual distribution of hydrogen production conversion efficiencies from on-site hydrogen production. Average WTW GHGs for the Learning Demonstration fleet operating on hydrogen produced from on-site natural gas reformation were 356 g CO₂-eq/mile and the lowest WTW GHG emissions for on-site natural gas reformation were 237 g CO₂-eq/mile. For the Learning Demonstration fleet operating on hydrogen produced from on-site water electrolysis (including some renewable sources of electricity), average WTW GHG emissions were 380 g

Learning Demonstration Fuel Cycle Well-to-Wheels Greenhouse Gas Emissions

FIGURE 7. Learning Demonstration Vehicle GHGs Using Actual Production Efficiencies and Fuel Economies

CO₂-eq/mile, with the lowest emissions estimated to be 222 g CO₂-eq/mile for the month with the best electrolysis production conversion efficiency.

Conclusions and Future Directions

- Completed the first four years of the five-year project with 140 vehicles now in fleet operation, 20 project refueling stations in use, and no major safety problems encountered.
- Analyzed data from 395,000 individual vehicle trips covering 1.9 million miles traveled and 90,000 kg H₂ produced or dispensed.
- Analyzed fuel cell system efficiency at 1/4-power and compared it to DOE target of 60%: system efficiency results from the four teams ranged between 52.5% and 58.1%.
- Published 60 CDPs to date and made them directly accessible to the public from a NREL's Web site.
- Continued to examine individual fuel cell stack degradation with each team to understand the results and refine both the inputs and the analysis performed.
- We will create new and updated CDPs based on data through June 2009 (Fall 2009 CDPs) and present results for publication at 2009 Fuel Cell Seminar.
- NREL will support key September 2009 DOE MYRDDP and Joule milestones on:
 - Hydrogen production cost from project compared to \$3/gge target.
 - Generation 2 stack voltage degradation time to 10% compared to target of 2,000 hours.

- Generation 2 vehicle freeze capability and start-up energy requirements compared to targets.
- We will support vehicle manufacturers, energy companies, and state organizations in California in coordinating early infrastructure plans.
- NREL will continue to identify opportunities to feed findings from the project back into Vehicle Technologies and Hydrogen Programs and industry R&D activities to maintain the project as a “learning demonstration.”
- We will publish the Spring 2010 and Fall 2010 composite data products as the last two sets of anticipated analysis results from the project.
- As the last deliverable from this project, we will write a final comprehensive summary report for publication.

Special Recognitions & Awards/Patents Issued

1. Nominated for “Best Dialogue Presentation Award” at the EVS-24 international vehicle conference in Stavanger Norway, April 2009 (one of only five posters nominated for this award out of hundreds).
2. Received 2009 DOE Hydrogen Program R&D Award, “In Recognition of Outstanding Contributions to the National Hydrogen Learning Demonstration,” May 2009.

FY 2009 Publications/Presentations

1. Kurtz, J., Wipke, K., Sprik, S., “Fuel Cell Vehicle Learning Demonstration: Study of Factors Affecting Fuel Cell Degradation,” Sixth International Fuel Cell Science, Engineering and Technology Conference (ASME Fuel Cell Conference), Denver, CO, June 2008. (paper and presentation).
2. Wipke, K., presentation of Learning Demonstration results to FreedomCAR Fuel Cell Tech Team, July 2008.
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4. Wipke, K., Sprik, S., Kurtz, J., Garbak, J., “Fuel Cell Vehicle Infrastructure Learning Demonstration: Status and Results,” *ECS Transactions: Proton Exchange Membrane Fuel Cells* 8, September 2008.
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VIII.2 Controlled Hydrogen Fleet and Infrastructure Demonstration and Validation Project

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Contract Number: DE-FC36-04GO14286

Subcontractors:

- Hyundai Motor Company (HMC), Seoul, South Korea
- Kia Motors Corporation (KMC), Seoul, South Korea
- Hyundai-KIA America Technical Center Inc. (HATCI), Chino, CA
- UTC Power (UTC), South Windsor, CT
- Alameda-Contra Costa Transit (ACT), Oakland, CA
- Southern California Edison (SCE), Rosemead, CA
- Gas Technology Institute (GTI), Des Plaines, IL

Start Date: January 15, 2004

Projected End Date: September 30, 2009

Objectives

- Validate performance targets:
 - Fuel cell stack durability: >2,000 hours
 - Vehicle range: >250 miles
 - Hydrogen cost: <\$3.00/gge
 - Safe and convenient refueling by drivers (with training).
- Demonstrate a variety of hydrogen generation technologies including:
 - Auto-thermal reformation of natural gas,
 - Low pressure steam reformation of natural gas,
 - High pressure steam reformation of natural gas, and
 - Electrolysis of water.

Technical Barriers

This project addresses the technical barriers from the Technology Validation section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) Lack of Fuel Cell Vehicle Performance and Durability Data
- (B) Hydrogen Storage
- (C) Lack of Hydrogen Refueling Infrastructure Performance and Availability Data
- (D) Maintenance and Training Facilities
- (I) Hydrogen and Electricity Co-Production

Contribution to Achievement of DOE Technology Validation Milestones

This project will contribute to achievement of the following DOE milestones from the Technology Validation section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- **Milestone 10:** Validate FCVs 2,000-hour fuel cell durability, using fuel cell degradation data. (4Q, 2009)
- **Milestone 12:** Validate cold start capability at -20 C. (2Q, 2011)
- **Milestone 14:** Validate achievement of a refueling time of 3 minutes or less for 5 kg of hydrogen at 5,000 psi using advanced communication technology. (2Q, 2012)
- **Milestone 22:** Five stations and two maintenance facilities constructed with advanced sensor systems and operating procedures. (4Q, 2006)
- **Milestone 23:** Total of 10 stations constructed with advanced sensor systems and operating procedures. (1Q, 2008)

Accomplishments

- All 32 vehicles have entered the project.
- One additional vehicle was added to the project.
- Five infrastructure stations continue safe operation.
- Two maintenance facilities continue safe operation.
- Safe and convenient refueling by drivers has been demonstrated.
- Cold weather vehicle testing has been completed.
- Survey of fuel cell vehicle drivers conducted.

Introduction

As a result of the President's Initiative, the DOE recently detailed a strategy to develop a hydrogen economy that emphasizes co-developing hydrogen infrastructure in parallel with hydrogen fuel cell-powered vehicles to allow a commercialization decision by 2015. In the past, efforts to introduce new energy technologies in the transportation sector have been thwarted by the classic "chicken and egg" dilemma of which comes first; in this case, hydrogen infrastructure or hydrogen vehicles. The Controlled Hydrogen Fleet and Infrastructure Demonstration and Validation project will be an important first step towards achieving the above strategy because the selected consortia will develop a complete system solution(s) that will address all elements of infrastructure and vehicle development.

These goals will be accomplished by developing hydrogen infrastructures and operating hydrogen-powered vehicles at selected U.S. locations.

Approach

CTV and its project team of HMC, HATCI, UTC and the site hosts intend to operate a fully integrated fueling and fleet operation consisting of 32 fuel cell vehicles, (including two different generations) with the aim of developing a database of operational experience under a wide variety of conditions including, for the stations, different technology and feed stocks, and for the vehicles, differing driving patterns and ambient temperatures. This data will also be collected in a manner that allows 'consumer' (including station operators, fuelers, drivers and maintenance workers) feedback to be recognized and incorporated into lessons learned.

Learnings from the early phases of this project can be incorporated into later phases in a way that allows performance improving technologies to be tested in the most cost-effective and efficacious manner.

Results

In support of DOE's objective "By 2009, validate 2,000-hour fuel cell durability in vehicles . . .", the fuel cell vehicles continue real world operation accumulating road hours, Figure 1. On-road vehicle data of fuel cell operating hours is being reported to the National Renewable Energy Laboratory (NREL) monthly. Five vehicles are currently operating at the cold weather station in Selfridge, Michigan and were subject to cold starts in the winter of 2008/2009 to validate cold start capability. Vehicles were left outside overnight prior to starting, Figure 2. Hyundai is addressing the barrier of

FIGURE 1. Vehicle FJM5

FIGURE 2. Cold Weather Start-Up

"Lack of facilities for maintaining hydrogen vehicles" by operating three maintenance facilities including the training of operators to maintain the vehicles. Training was also conducted for first responders at all stations. In addition refresher training is offered each year to local first responders to support the training of new responders to the communities around the hydrogen stations, Figure 3.

In support of DOE's objective "By 2009, . . . safe and convenient refueling by drivers (with training), Chevron has been training drivers to conduct fueling of the fuel cell vehicles. Drivers have performed hundreds of safe refueling events at several infrastructure stations 24/7, Figure 4.

Chevron is operating five stations in support of DOE's objective "By 2009, . . . validate hydrogen infrastructure that results in a hydrogen production cost of less than \$3.00/gge (untaxed) delivered". Data from operating these stations is provided to NREL and is stored at the Hydrogen Secure Data Facility in Golden, CO. A hydrogen energy station continues to operate at the Hyundai-Kia America Technical Center in Chino,

FIGURE 3. Driver Training **FIGURE 4.** First Responder Refresher Training

California. This station demonstrates the on-site auto-thermal reformation of natural gas. This Chino site serves as the commissioning site for all project vehicles as well as one of the project's fleet operators. The station, as all stations in the project, was designed to utilize state-of-the art remote monitoring and operation systems and incorporates advanced hydrogen and fire sensors. A hydrogen energy station continues to operate

at Alameda-Contra Costa Transit in Oakland, California. This station has been only partially funded by the DOE project but the data from this station is being shared with NREL. This station demonstrates the use of on-site low-pressure and high-pressure steam methane reforming.

A hydrogen energy station has been installed at the Progress Energy site in Orlando, Florida. This station has not been funded by DOE but CTV will report the station data to NREL. A hydrogen energy station continues operation at the SCE site in Rosemead, California. This site demonstrates on-site production of hydrogen using electrolysis. A cold weather hydrogen energy station continues operation at the Selfridge Air National Guard site in Selfridge, Michigan.

To address DOE's barrier of hydrogen and electricity co-production, the Gas Technology Institute has constructed a partial oxidation gas turbine. This system will be capable of producing hydrogen and electricity. A partial oxidation reactor will be used to generate hydrogen. Electricity will be generated with a turbine and a slip stream will be sent to a water-gas shift reactor to increase the concentration of hydrogen in the gas stream.

Conclusions and Future Directions

Thirty-two vehicles have been entered into the project. One additional vehicle has been added and 14 vehicles have been retired. Five hydrogen infrastructure stations have been placed into operation.

The project will continue to operate vehicles and infrastructure in real world settings while reporting data to NREL.

FY 2009 Publications/Presentations

1. Controlled Hydrogen Fleet and Infrastructure Demonstration and Validation Project 2009 Annual Merit Review Presentation.

VIII.3 Hydrogen Fuel Cell Vehicle & Infrastructure Demonstration Program Review

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Contract Number: DE-FC36-04GO14287

Subcontractor:
BP America Inc., Naperville, IL

Start Date: November 17, 2004
Projected End Date: April, 2010

Objectives

Ford:

- Gain vehicle operational data in differing climate conditions, to direct and augment future design efforts.
- Provide input to the industry-government efforts to define a future hydrogen economy.

BP:

- Provide safe, reliable user friendly hydrogen infrastructure.
- Install technology to meet cost targets.
- Test a variety of hydrogen delivery options.

Technical Barriers

This project addresses the following technical barriers identified in the Technology Validation section (3.6.4) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan (October 10, 2007, update April 2009):

- (A) Lack of Fuel Cell Vehicle Performance and Durability Data
- (B) Hydrogen Storage
- (C) Lack of Hydrogen Refueling Infrastructure Performance and Availability Data
- (D) Maintenance and Training Facilities
- (E) Codes and Standards

Contribution to Achievement of DOE Technology Validation Milestones

This project will contribute to achievement of the following DOE Technology Validation milestones from the Technology Validation section (3.6.6) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- **Milestone 2:** Demonstrate FCVs that achieve 50% higher fuel economy than gasoline vehicles (3Q, 2005).
- **Milestone 4:** Operate fuel cell vehicle fleets to determine if 1,000 hours fuel cell durability, using fuel cell degradation data, was achieved by industry (4Q, 2006).
- **Milestone 5:** Validate vehicle refueling time of 5 minutes or less for a 5 kg tank (1 kg/min). (4Q, 2006).
- **Milestone 7:** Validate vehicle refueling time of 5 minutes or less for a 5 kg tank (1 kg/min) at 5,000 psi through the use of advanced communications technology. (4Q, 2007).
- **Milestone 8:** Fuel cell vehicles demonstrate the ability to achieve 250-mile range without impacting passenger cargo compartment (4Q, 2008).
- **Milestone 10:** Validate FCVs 2,000-hour fuel cell durability, using fuel cell degradation data. (4Q, 2009)
- **Milestone 22:** Five fueling stations and two vehicle maintenance facilities constructed using advanced sensor systems and operating procedures (YE 2006).
- **Milestone 23:** Total of 10 stations constructed with advanced sensor systems and operating procedures. (1Q, 2008)
- **Milestone 24:** Validate a hydrogen cost of \$3.00/gge (based on volume production) (4Q, 2009).

Accomplishments

- As reported in 2005, dynamometer testing confirms 50% higher fuel economy and indicates that the target set in this program Milestone 2 has been met.
- 1,000-hour durability has been demonstrated in on-road durability testing. The 18-car demonstration fleet has exceeded this Milestone target.
- Average data in 2009 for both communications and non-communications fueling fill-ups indicates an average fill rate of more than 1.1 kg/min which meets the Milestone 5 target.
- Fill times of 5 minutes or less have been demonstrated for ‘full’ fills using vehicle-to-station communication. Milestone 7 has been met.
- As detailed in earlier reports, Ford’s Technology Demonstrator Vehicle (TDV) program of progressive design levels demonstrating improved range in functional configurations (Table 1) has demonstrated capability for the targeted 250-mile range, in a sport utility vehicle (SUV) configuration with slightly reduced passenger volume, and also in a plug-in hybrid fuel cell cross-over vehicle with little passenger compartment compromise.
- Ford is submitting ongoing field vehicle data in support of Milestone 10.
- In support of Milestone 22:
 - Service Facilities: As previously reported, Ford has completed two service facilities for project vehicles in Dearborn, MI, and Sacramento, CA. In Florida, repair work is being performed in a nearby, cooperating Ford dealership. A fourth service operation has been opened in Reykjavik, Iceland. All facilities utilize state-of-the-art hydrogen sensors, and have service and operating procedures established for hydrogen-fueled vehicles. Hundreds of operators and emergency responders have been trained in safe operation and approaches to hydrogen powered vehicles.

- Fueling Stations: In Michigan BP began operation of the City of Taylor (CoT) hydrogen liquid delivery station in October 2006. In Florida, construction and installation of the electrolysis hydrogen station was completed in April 2007. In California, the renewable hydrogen generation station at Sacramento Municipal Utility District (SMUD) opened in March 2008. The 700 bar upgrade of the Ford Dearborn station is operational. BP completed three stations and an upgrade to the Dearborn station for 700 bar fueling.
- As previously reported, BP has assessed, through meetings with suppliers, several technologies to understand the current status and potential for meeting the \$3.00/gasoline gallon equivalent (gge) target untaxed by 2009. Their study concluded that the H2Gen 2000 and the Air Products Harvester units could meet the \$3.00/gge untaxed hydrogen production cost target using the H2A model assumptions. BP will not provide independent verification.

Since the last annual report, specific accomplishments in this technology demonstration are:

- Fleet vehicle operation continued past the original 36-month operation and will continue to supply data until September 30, 2009. Eleven vehicles will have operated for 48 months.
- Fueling fill times that meet the program milestone target of five minutes or less continue to be demonstrated.
- Technology demonstrator vehicles have been used to certify and demonstrate effective 700 bar fuel systems, both on vehicle and in the fueling station.

TABLE 1. Technology Demonstration Vehicle Plan

Vehicle Attributes	H2 Storage Upgrade	Robustness Demonstrator	Designed Around Hydrogen Demonstrator	Flexible Series H2 Hybrid
Fuel Cell Generation	Gen 1	Gen 2 (Stage 1)	Gen 2/3 (Stage 2)	APU
Number of Vehicles	1	1	3	1
Range (miles)	240	200	>300	300
Hydrogen Storage (bar)	700	350	350 & 700	350
Unassisted Cold Start	2°C	2°C	< 0°C	-15°C
Assisted Cold Start	2°C	2°C	-15°C	-25°C
Fuel Efficiency (mpg) (*normalized to Focus)	50	50	50	40-70

Introduction

In order to meet the objectives and deliverables of this technology demonstration project, Ford and BP developed an approach that permits demonstration of the current state of technology while continuing to develop and prepare demonstrations of newly emerging technologies and techniques. In this approach, Ford has deployed 18 vehicles, powered by a Ballard Mark 902 fuel cell system, in customer fleet applications. DOE requested data describing operating parameters is being collected using computerized, automated data collection and analysis techniques. At the same time, new concepts of vehicle and component design are being developed using emerging technologies to demonstrate progress toward the DOE's longer-term milestones and targets.

The original plan defined the fleet operational period to be 36 months per car. Based on the value of data that is being collected and the learning from high hour fuel cell stack data, Ford, BP and the DOE had agreed to continue field operations through the end December, 2009. However, late changes by BP have caused the demonstration end date to be moved forward to September 30, 2009.

At the beginning of the vehicle demonstration, BP first deployed delivered hydrogen to permit fleet operations. With initial fleet deployment complete, BP worked with local authorities where the cars are operating, to locate, plan and certify hydrogen fueling stations in each of the fleet operating areas.

Approach

The Ford vehicle demonstration approach utilizes two phases: 1) deployment of 18 customer-operated vehicles in three different geographic and climatic areas (California, Florida and Michigan) and 2) development of TDVs that incorporate advanced technology and design concepts directed at meeting future DOE targets for improved hydrogen storage and interface, durability, low temperature operation, fuel economy, range and reduced weight and cost.

BP's infrastructure approach followed in two phases: 1) test infrastructure deployment by installing hydrogen delivered stations, including electronic data collection for select sites, and 2) assessing the ability to meet cost targets by installing onsite renewable hydrogen electrolysis production and/or 700 bar fueling at select sites. Completed station installations include CoT, Michigan, Florida Progress Energy, Orlando, and SMUD, Sacramento, California. 700 bar capability was made available at the Ford Dearborn site.

Results

The vehicles are operating efficiently (meeting fuel consumption targets) and effectively (vehicle "up-time" in excess of 95%). The fleet and involved personnel have also continued to demonstrate a 100% safety performance with no incidents or near misses. Six second-phase demonstrators are built and have demonstrated new concepts for packaging of the various system components for improved performance, range and noise reductions. Two vehicles are operating with 700 bar fuel systems

Three hydrogen fueling stations are operating. The CoT station has presented challenges with dispenser and compressor reliability. Problems continue and have increased as the station ages. Although the Jamestown station was commissioned in June 2007, problems with the nine electrolyser power supplies caused the station to use delivered hydrogen until January 2008. It has performed well since the reopening. The SMUD renewable hydrogen station opened in March 2008 and has operated efficiently.

Conclusions and Future Direction

The project is providing important data on both vehicle performance and infrastructure development. Three configurations of fuel cell vehicles, a passenger car, an SUV and a cross-over continue to demonstrate useable customer designs with some compromise for passengers. 700 bar fuel storage has been successfully implemented in vehicles and a station. Data collection will continue through September 30, 2009 for the 18 customer vehicles, providing the required data to support the program milestones.

The Jamestown, CoT and SMUD stations have presented an opportunity to better understand the differences in support service from a variety of gas and equipment suppliers, as well as offer comparisons between renewable and non-renewable hydrogen generation, or delivered vs. distributed production. Although the Dearborn 700 bar station is complete, the short time remaining in the demonstration minimizes the opportunity to gather and share relevant operational data.

With the decommissioning of the three fleet fueling stations, the fleet demonstration project will come to an end and final technical reporting will be prepared. The final technical report will be submitted early in 2010. Ongoing TDV evaluation data will continue to be shared with the DOE until such time as the DOE and Ford determine that the effort should terminate.

VIII.4 Hydrogen to the Highways

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Contract Number: DE-FC36-04GO14285

Subcontractors:

- Daimler, Stuttgart, Germany
- BP America, Warrenville, IL
- Mercedes-Benz USA LLC, Montvale, NJ
- DTE Energy, Detroit, MI
- NextEnergy, Detroit, MI
- Automotive Fuel Cell Cooperation (AFCC), Vancouver, BC

Start Date: December 22, 2004
Projected End Date: September 30, 2009

Objectives

- Record, collect and report data from fuel cell vehicles (FCVs) and the hydrogen fueling operations to validate 2009 Department of Energy (DOE) targets:
 - Fuel cell stack durability: 2,000 hours
 - Vehicle range: +250 miles
 - Hydrogen cost at the station: \$3.00/gge
- Demonstrate the safe installation of hydrogen fueling stations and fuel cell service facilities as well as the safe operation of all fuel cell vehicles.
- Raise public awareness of hydrogen technology and demonstration projects.
- Establish an initial hydrogen infrastructure network to support a small fleet of fuel cell vehicles.
- Develop codes and standards and implement rigorous safety processes.
- Explore cost and commercial feasibility of renewable-based hydrogen generation.

Technical Barriers

This project addresses the following technical barriers from the Technology Validation section (3.6.4) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) Lack of Fuel Cell Vehicle Performance and Durability Data
- (B) Hydrogen Storage
- (C) Lack of Hydrogen Refueling Infrastructure Performance and Availability Data
- (D) Maintenance and Training Facilities
- (E) Codes and Standards
- (H) Hydrogen from Renewable Resources

Contribution to Achievement of DOE Technology Validation Milestones

This project will contribute to achievement of the following DOE technology validation milestones from the Technology Validation section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- **Milestone 4:** Operate fuel cell vehicle fleets to determine if 1,000 hour fuel cell durability, using fuel cell degradation data, was achieved by industry. (4Q2006)
- **Milestone 7:** Validate vehicle refueling time of 5 minutes or less for a 5 kg of hydrogen (1kg/min) at 5,000 psi through the use of advanced communication technology. (4Q2007)
- **Milestone 8:** Demonstrate the ability to achieve 250 mile range without impacting passenger cargo compartment. (4Q2008)
- **Milestone 10:** Validate FCV's 2,000 hour fuel cell durability using fuel cell degradation data. (4Q2009)

Accomplishments

- Continued mileage accumulation through customer operations with vehicles in service for over 5 years.
- Upgraded and operated Gen I vehicles with 70 MPa tank system as well as optimized and tested Gen II's computer processing unit (CPU) software to further improve fuel economy and start-up time.
- Submitted over 85 DVDs of raw data to National Renewable Energy Laboratory (NREL).
- Embraced DOE's "lighthouse" vision by relocating primary workshop from West Sacramento to Long Beach, California.

- Completed construction of City of Burbank station with infrared data acquisition (IRDA) communication as well as 35 MPa and 70 MPa fueling dispenser.
- Installed new electrolyzer and dispenser at the DTE Hydrogen Technology Park.
- Internally operated Gen II pre-production vehicles in a variety of driving patterns and weather conditions.

Introduction

The primary goal of this project is to validate fuel cell technologies for infrastructure, transportation as well as assess technology/commercial readiness for the market. The Chrysler Team, together with its partners, have been testing the technology by operating and fueling hydrogen fuel cell vehicles under real world conditions in varying climate, terrain and driving conditions. Vehicle infrastructure data has been collected to monitor the progress toward the 2009 hydrogen vehicle and infrastructure performance targets of \$2.50–3.00/gge hydrogen production cost and 2,000-hour fuel cell durability. Furthermore, progress is being made to validate a greater than 250-mile range without impacting the passenger or cargo compartments. Finally, to prepare the public for a hydrogen economy, outreach activities have been designated to promote awareness and acceptance of hydrogen technology.

Approach

To achieve the project goals, the Chrysler Team deployed 30 Gen I vehicles into customer hands for real-world operations in three climatic regions of the United States. The Team is also providing data from Gen II vehicles under the similar operations as Gen I vehicles to compare technology maturity during program duration. All vehicles have been equipped with a data acquisition system that automatically collects statistically relevant data for submission to NREL, which monitors the progress of the fuel cell vehicles against the DOE technology validation milestones. The energy partners, BP, DTE, and NextEnergy, have installed an infrastructure to provide hydrogen to the Chrysler Team's FCVs and to evaluate the technologies which have the potential to achieve the DOE hydrogen cost targets.

To raise public awareness of hydrogen technology and demonstration projects, the Chrysler Team aligned its communication activities with the goals of the DOE. In addition, project safety was maintained through continued inter-team communication, vehicle and infrastructure training, employee and customer

education, “tabletop” incident management drills and emergency responders training.

Results

Gen I Fuel Cell (F-Cell) Vehicles

Although the F-Cell fleet was originally intended for a 2-year operation, A-Class F-Cells have outperformed engineering expectations as the vehicles have been in full operation for over five years. Since the inception of the demonstration project, customers have driven over 300,000 miles, allowing the Chrysler Team to generate over 85 DVDs of raw data for submission to DOE. One fuel cell vehicle was deployed to NREL at Golden, Colorado for the laboratory's Advanced Technology Fleet Effort (see Figure 1).

To embrace DOE's “lighthouse” vision, the primary workshop was relocated from Sacramento to Long Beach, California. One service center remains in Palo Alto for Northern California customer support. The move to Southern California provided an impetus to more closely analyze the infrastructure landscape and station access for near-future fuel cell vehicle commercialization as well as for immediate need to fuel 70 MPa vehicles for testing and operating purposes.

Multiple Gen I A-Class F-Cells have been upgraded with new 70 MPa tank systems and corresponding components such as pipes, valves and tank controller units. The vehicles began internal operations in Southern California so that the 70 MPa Burbank hydrogen fueling station may be utilized and vehicle/infrastructure data may be collected and submitted to NREL.

Further progress was made toward the development of the start/stop software, designed to improve fuel economy by disconnecting the fuel cell stack during idle phase. Several Gen I vehicles were flashed with the start/stop software and were tested through extensive cycles. The test results clearly showed a positive effect on the vehicle's performance, especially on fuel consumption.

FIGURE 1. Gen I F-Cell Utilized by NREL

Gen II Technical Accomplishments

Start/stop software improvements were also developed for second generation vehicles, or B-Class F-Cells. The new Gen II start/stop algorithm optimized the interface between the fuel cell and energy management system, thereby decreasing the time to restart the fuel cell system after being disconnected. This software has already been integrated into the design and verification process.

To expeditiously provide DOE with data generated from the fuel cell system designed for the second generation vehicle, Gen II fuel cell vehicles were tested on a dynamometer so that fuel economy and range could be verified. In addition, Gen II fuel cell systems were evaluated on a test bench to simulate 2,000 hours of real world driving conditions. The fuel cell system performed well under the stringent test conditions and the processed data has been submitted to NREL for analysis.

To complement the fuel cell system testing, internal Gen II vehicle operations were performed under a wide range of terrain and climate conditions, including diverse temperature, humidity and ambient air pressure (see Figures 2 and 3). For example, Gen II vehicles were driven in extreme cold weather conditions with temperatures as low as -26°C and met all engineering requirements, including reliability and durability. In addition, the Chrysler Team internally operated Gen II vehicles in the hot and dry conditions of Death Valley. While the vehicles performed up to customer expectations, valuable insight was gained and a variety of on-road vehicle data was collected. Raw data from internal operation in Death Valley, as well as other locations, have been submitted to NREL. This allowed the research facility to validate the 2009 DOE targets.

FIGURE 2. Gen II Fuel Cell Vehicles Operated in Cold Weather

FIGURE 3. Hot Weather Testing of Gen II B-Class

Codes and Standards

The Chrysler Team participated in various working groups to support and assist with the development of codes and standards. Of particular note is Society of Automotive Engineers (SAE) J2578 (“Recommended Practice for General Fuel Cell Vehicle Safety”) and SAE J2579 (“Technical Information Report for Fuel Systems in Fuel Cell and Other H₂ Vehicles”) that have been discussed in the SAE Safety Working Group and have been revised for publication. The draft of SAE J2601, which provides fueling protocol methodology for pressures up to 70 MPa, will be published in 2009 so that it may replace the document commonly known as Next Energy Release A document. The U.S. National Highway Traffic Safety Administration will modify the Federal Motor Vehicle Safety Standards (FMVSS) to ensure that safety practices adhered by fuel cell vehicle manufacturers are consistent with the processes specified in FMVSS 305.

NextEnergy Center held its Hydrogen Codes and Standards Conference which attracted first responders, local officials, hydrogen industry experts, and national code development organizations that provided updates on the latest developments of national and international hydrogen codes and standards. This conference featured updates from such organizations as SAE, American Society of Mechanical Engineers, Canadian Standards Association America, Compressed Gas Association, International Code Council, and International Organization for Standardization.

Safety and Health

On-going safety and health programs were maintained with no major hydrogen-related events to report. The 2008 to 2009 reporting period began with emergency responder training in Santa Clara County and commissioning of the Palo Alto maintenance facility as well as hydrogen training for all on-site staff. In

addition, the vehicle lift grounding system was updated at all maintenance facilities.

The Chrysler Team, in conjunction with City of Burbank, finalized the risk assessment activities including Hazards and Operational Safety Analysis/ Hazard Identification Analysis studies for the 70 MPa Burbank hydrogen fueling station in California. Information gathered during the risk assessment process was incorporated into the National Environmental Policy Act (NEPA) and California Environmental Quality Act (CEQA) process where applicable.

Outreach and Media

Early in the year, the Chrysler Team participated in traditional outreach events such as the SAE World Congress in Detroit and the National Hydrogen Association meeting in Sacramento where the F-600 cutaway model and a newly designed well-to-wheels kiosk were displayed. Other customary events of which the Chrysler Team was a part included the ride-n-drive at the Fuel Cell Seminar in Phoenix, and the Electric Drive Transportation Association (EDTA) Exposition in Washington, D.C. where the upgraded 70 MPa A-Class F-Cell was on display, together with banners describing the Chrysler Team's partnership with the DOE. The largest outreach event in 2008 was the Hydrogen Road Tour spearheaded by the Department of Transportation.

Fueling Stations and Co-Production Facilities

Burbank Station

With significant cooperation from a wide variety of partners, including the City of Burbank, California Air Quality Management District and DOE, the Chrysler Team fulfilled its commitment to complete the construction and commissioning of the Burbank hydrogen fueling station (see Figure 4). Not only were the NEPA/CEQA, local permitting requirement and legal agreement with the City of Burbank completed, but all the functionality of all components, including the steam methane reformer, was confirmed. The fueling system was filled with hydrogen from a tube trailer, and is presently filling 35 MPa cars that the City of Burbank operates. In addition, several 70 MPa vehicles with an IRDA system were fueled to full capacity.

DTE Hydrogen Technology Park

To keep up with the cold weather demands of Michigan, the electrolyzer and dispenser of the fueling station were replaced. The dispenser was modified to accept 70 MPa vehicles for communicated fills. While the manufacturer completed installation, testing and start up during the fourth quarter of 2008, Michigan

FIGURE 4. Burbank Hydrogen 35 MPa and 70 MPa Fueling Station

Department of Environmental Quality final inspection was finalized during the third quarter of 2009. The DTE Energy Hydrogen Technology Park is currently up and running doing vehicle fueling.

Los Angeles International Airport (LAX)

While the site had not been funded under the current DOE grant, it regularly served Daimler/Chrysler/DOE customers as well as Ford, Toyota and Honda. BP terminated its operation of the Praxair LAX station during the third quarter of 2008. BP de-branded the station and the site remained available to customers that had contracts with Praxair until the second quarter of 2009.

NextEnergy

BP and its partners have agreed to transfer the station assets and operating responsibility to NextEnergy. The station is open and functioning well. NextEnergy Center presently has fueling agreements with several original equipment manufacturers (OEMs) to refuel hydrogen vehicles.

Critical Infrastructure Next Steps

As fuel cell vehicles transition from a demonstration phase to commercialization, the development of well established hydrogen fueling station network is critical and, as a result, the following recommendations are made:

- More funding must be devoted toward long-term infrastructure development.
- Forty hydrogen stations need to be placed in the Los Angeles area by 2010.
- Station deployment should consider the needs of all fleets operating under the program.

- All new stations must meet the performance specifications outlined in the NextEnergy Release A document.
- To ensure maximum vehicle utilization, fuel costs must be considered.

Summary and Future Directions

Summary

- Completed construction of City of Burbank 70 MPa station.
- Installed new electrolyzer and dispenser at DTE Station.
- Internally operated Gen II pre-production vehicles.
- Upgraded and operated vehicles with 70 MPa tank system and new CPU software.
- Continued mileage accumulation of Gen I vehicles.

Future Work

- Prepare for next generation demonstrations.
- Work with DOE to ensure existing hydrogen stations remain open and available.
- Finalize decision and plan for project extension.
- Maintain smooth operation of Gen I fuel cell vehicles with on-going service, maintenance and customer support.
- Continue internal operations of Gen II vehicles.
- Maintain the high quality of technical vehicle and infrastructure data reporting to NREL/DOE.
- Pursue novel approaches toward outreach and media events to raise public knowledge of hydrogen technology and demonstration projects.

Hydrogen Stations

Placing a hydrogen fueling station is a unique experience that breaks new ground. Based on the experiences and lessons learned from the City of Burbank station, the following conclusions and recommendations are made:

- OEM and energy company coordination is important for optimal selection of sites.
- Funding for long-term operation needs to be discussed.

- Reformer supplied facilities were much more complex and required larger footprint than anticipated.
- Early coordination with officials to establish relationships is critical.
- Additional documentation and unexpected requirements from permitting officials are not unusual.
- NEPA/CEQA process can be very lengthy and interfere with budget deadlines.
- Legal contracts often take much longer than expected.
- Reliability of equipment needs to be improved.
- A better set of analytical test methods is needed to ensure hydrogen quality.

Publications/Presentations

Below is a list of presentations made by the Chrysler Team:

Fuel Cell 2008; Long Beach, CA	05/08
Memorial Day Parade; Scotch Plains, NJ	06/08
Turner Logistics Tradeshow; Long Beach, CA	07/08
Aspen Ideas Festival; Aspen, CO	07/08
Semicon West; San Francisco, CA	07/08
John Mayer Concert; Jones Beach, NY	08/08
Butterfly Festival; Trenton, NJ	08/08
Hydrogen Drive; Maine to California	10/08
California Science Teacher's Association Conference; San Jose, CA	12/08
EDTA Conference and Expo; Washington, DC	04/08
World Mobility Forum; Stuttgart, Germany	01/09
Firehouse World; San Diego, CA	02/09
Washington DC Auto Show; Washington, DC	02/09
Alternative Fuels Symposium – 2 nd annual Meeting; Paris, France	03/09
20 th NHA Conference and Hydrogen Expo; Columbia, SC	03/09
NAFA Annual Convention; New Orleans, LA	04/09
NAFA March Meeting; New York, NY	05/09
EVS-24: The International Battery, Hybrid and Fuel Cell Electric Vehicle Symposium; Stavanger, Norway	05/09

VIII.5 Hydrogen Vehicle and Infrastructure Demonstration and Validation

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Contract Number: DE-FC36-04GO14284

Phase 1 Partners:

- Shell Hydrogen, LLC, Houston, TX
- U.S. Army, Ft. Belvoir, VA
- Quantum Technologies, Inc., Irvine, CA
- Viewpoint Systems Inc., Rochester, NY
- NextEnergy, Detroit, MI
- U.S. Environmental Protection Agency, Washington, D.C.
- District of Columbia Department of Transportation, Washington, D.C.
- Virginia Department of Environmental Quality, Richmond, VA
- U.S. Postal Service, Washington, D.C. and Irvine, CA

Phase 2 Partners:

- Project Driveway drivers composed of media, policy makers, general public, businesses, and government

Project Start Date: October 1, 2004

Project End Date: September 30, 2009

Objectives

General Motors (GM) and energy partner Shell Hydrogen, LLC, are deploying a system of hydrogen fuel cell electric vehicles (FCEVs) integrated with a hydrogen fueling infrastructure to operate under real world conditions:

- Demonstrate progressive generations of fuel cell system technology.
- Demonstrate multiple approaches to hydrogen generation and delivery for vehicle fueling.
- Collect and report operating data.

Technical Barriers

Project addresses the following technical barriers from the Technology Validation section (3.6.4) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) Lack of Fuel Cell Electric Vehicle Performance and Durability Data
- (C) Lack of Hydrogen Fueling Infrastructure Performance and Availability Data
- (D) Maintenance and Training Facilities
- (E) Codes and Standards

Contribution to Achievement of DOE Technology Validation Milestones

This project contributes to the achievement of the DOE Technology Validation milestones listed below from the Technology Validation section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- **Milestone 2:** Demonstrate FCEVs that achieve 50% higher fuel economy than gasoline vehicles. (3Q, 2005)
- **Milestone 4:** Operate fuel cell vehicle fleets to determine if 1,000-hour fuel cell durability, using fuel cell degradation data, was achieved by industry. (4Q, 2006)
- **Milestone 22:** Five stations and two maintenance facilities constructed with advanced sensor systems and operating procedures. (4Q, 2006)

Accomplishments

GM has accomplished the following project milestones:

- Deployed 50 vehicles demonstrating two generations of GM's proprietary fuel cell technology in various terrains, driving conditions, and climates including cold weather:
 - FCEV fleet included eight Phase 1 HydroGen3 FCEVs and 42 Phase 2 Chevrolet Equinox FCEVs (see Figure 1) employing GM's proprietary 3rd and 4th generation fuel cell (FC) technology.
- Constructed and utilized first class maintenance and training facilities located in Ardsley, NY, Ft. Belvoir, VA and Burbank, CA with a satellite hub located in Lake Forest, CA:

FIGURE 1. Chevrolet Equinox Fuel Cell Electric Vehicles

- Over 1,500 first responders received safety training through these facilities.
- Drivers receive first class customer service through the use of driver relationship managers and the On-Star call center providing 24-hour, 365-day support.
- Established retail and retail-like hydrogen stations for public fueling:
 - Seven fueling stations in operation spreading across the eastern and western regions with two additional stations to open in the 3rd quarter of 2009.
 - Different types of hydrogen generation/delivery options are demonstrated such as delivered compressed gas and on-site electrolysis.
 - Two stations are infrared capable and able to fast-fill 3+ vehicles back-to-back.
 - H₂ quality testing has been completed in both eastern and western regions, among the first stations in the U.S. to be tested at 700 bar.
- Opened nation's first retail hydrogen fueling station located in Washington, D.C; station has been in use since November 2004 and was the first retail station in the U.S. equipped to fuel with hydrogen dispensed at 700 bar.
- Partnered in opening the first retail hydrogen fueling station in CA; located in Los Angeles it features on-site generation through a canopy-mounted electrolyzer.
- Commissioned two new hydrogen stations in the past year:
 - GM and Clean Energy station in Los Angeles, CA near the Los Angeles International Airport (LAX) opened in record time, in less than five months (see Figure 2).
 - GM, Shell Hydrogen and the Port Authority of New York-New Jersey collaborated to open a fueling station at the John F. Kennedy (JFK) airport in New York (see Figure 3).
- Gathered comprehensive feedback on all elements of customer experience and vehicle performance to guide future FCEV and infrastructure development.
- Collected vehicle and station data according to the National Renewable Energy Laboratory (NREL) data reporting templates using automated logbook

FIGURE 2. Clean Energy Station near LAX in Los Angeles, CA

FIGURE 3. Shell Hydrogen Station Located at JFK Airport

entry and automated wireless data transfer from vehicles to a data server:

- Transitioned seamlessly from Phase 1 to Phase 2 in data collection and vehicle testing overcoming the challenges of a new vehicle platform, new generation of FC technology and the increase from eight to 42 vehicles on the road.
- Conducted and verified extensive cold weather performance testing; additionally, vehicles were deployed in North East U.S. this winter and performed as customers expected (see Figure 4).

Introduction

As a part of this project, GM has deployed 50 FCEVs demonstrating two generations of proprietary FC technology over the past 5 years. Today, GM has retired the eight commercially developed FCEVs from Phase 1, according to plan. The 42 Phase 2 vehicles are deployed in the New York City metropolitan, Washington, D.C., and Los Angeles, CA areas. Four maintenance and training hubs are used to support these deployments.

FIGURE 4. Chevrolet Equinox FCEV Completing Cold Weather Testing

The vehicles are accumulating miles and generating data that is submitted according to the NREL data reporting templates.

Our partner, Shell Hydrogen, has opened hydrogen fueling stations which are available for all original equipment manufacturer FCEVs to use. Two additional stations are scheduled to open later this year, one in each region. Also, GM can fuel at GM maintenance and training sites and at the Clean Energy station in CA. The stations employ various forms of hydrogen generation and delivery options including delivered compressed gas and the world's first canopy-mounted electrolyzer. Data from retail station operation is recorded and submitted according to the NREL data reporting templates.

Approach

GM is currently demonstrating FCEVs through the deployment and testing of 42 FCEVs in various terrains, driving conditions, and climates including cold weather. The project approach is to establish and install retail hydrogen stations for public fueling on the East and West Coasts, as well as explore hydrogen generation/delivery options such as electrolysis. Service operations support these FCEVs with personnel trained in maintenance, fueling, technical support and safety. Project Driveway drivers can expect an exciting and confident driving experience through the utilization of locally-based GM Driver Relationship Managers and OnStar service.

Report data required under the project is generated through on-road and dynamometer test data captured from the vehicles, as well as from the hydrogen infrastructure production and fueling operation data. In addition to these efforts, NextEnergy will develop codes and standards permitting templates and a database of permitting experiences.

Results

Two generations of GM's proprietary FC technology have been demonstrated in diverse climates, driving conditions, and terrains with vehicle deployments on the east and west coasts. Data was collected from the

deployments during both phases and the transition from Phase 1 vehicles to Phase 2 vehicles was seamless in data collection and vehicle testing.

All Phase 2 vehicles are a part of the Chevrolet Project Driveway program which was designed to provide GM with comprehensive feedback on all elements of the customer experience and vehicle performance. All of our customers whether business-to-business, government, or general public have high praise for the first class customer-focused service provided in their vehicle experience.

Maintenance and training are ongoing at our four hydrogen-ready training and service facilities. Seven fueling sites in the New York City metropolitan and Southern California area have been constructed to support the fueling of the vehicles, with two additional sites to open later this year. The stations demonstrate different types of hydrogen generation/delivery options such as delivered compressed gas and on-site electrolysis, with all but one dispensing at 700 bar.

Key vehicle and infrastructure data generated and reported that support the milestones are stack durability, fuel economy and vehicle range, FC system efficiency, maintenance and safety, and fueling rate. Dynamometer testing, including end-of-life testing, of Phase 1 vehicles has been conducted at GM's Milford Proving Ground according to the DOE schedule. Phase 2 vehicles have gone through the beginning of life testing which included cold weather tests. On road data collection has been automated wherever possible.

The hydrogen orientation program for emergency first responders has now been delivered in cities where GM's DOE vehicles operate totaling over 1,500 people trained. NextEnergy Center is now chairing task groups made up of a consortium of industry experts on hydrogen to provide feedback on the National Fire Protection Agency hydrogen codes. NextEnergy Center has also successfully transferred its hydrogen permitting database tools to its new Web site.

Future Directions

- Provide ongoing support for the operation of 42 Phase 2 DOE Chevrolet Equinox FCEVs.
- Continue new driver training on FCEVs, hydrogen safety, and hydrogen fueling.
- Inaugurate usage of additional hydrogen fueling stations in the New York City metropolitan area and the West Los Angeles area, both capable of dispensing at 700 bar.
- Participate in the NextEnergy annual conference.
- Continue to collect, analyze, and report data from project vehicles and fueling locations and meet all project deliverables.

The commissioning of a facility that dispenses hydrogen is a unique experience and breaks new ground. Based on our experience and lessons learned to date, we are making the following infrastructure recommendations:

- Retail-Like Fueling Stations
 - Geographically targeted regions where automakers want to put vehicles.
 - 700 bar fast-fill fueling with infrared communication link.
 - Compelling station designs (customer and technology perspectives).
 - Robust hydrogen capacity and throughput – designed for growth.
 - Operational with (or before) vehicles – market enabler.
- Access to all Stations
 - All automotive companies and their customers have access.
 - Standard fueling protocol – safe/fast/effective fueling of all vehicles.
 - Address liability exposure – straight-forward access agreements with consistent principles, or eliminate access agreements all together.
- Expedient Station Approval and Permitting Process
 - State-wide consistency and local adherence.
 - Community support.
- Funding Support and Incentives
 - Stations, station technology, and capacity upgrades.
 - Liability coverage/solution (funded liability pool, liability cap).
 - Assurance stations will be there on time – supply base.

VIII.6 Validation of an Integrated Hydrogen Energy Station

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Contract Number: DE-FC36-01GO11087

Subcontractor:

FuelCell Energy, Danbury, CT

Start Date: September 30, 2001

Projected End Date: March 31, 2010

Objectives

Demonstrate the technical and economic viability of a hydrogen energy station using a high-temperature fuel cell designed to produce power and hydrogen.

- Complete a technical assessment and economic analysis on the use of high-temperature fuel cells, including solid oxide and molten carbonate, for the co-production of power and hydrogen (energy park concept).
- Build on the experience gained at the Las Vegas H2 Energy Station and compare/contrast the two approaches for co-production.
- Determine the applicability of co-production from a high-temperature fuel cell for the existing merchant hydrogen market and for the emerging hydrogen economy.
- Demonstrate the concept at a suitable site with demand for both hydrogen and electricity.
- Maintain safety as the top priority in the system design and operation.
- Obtain adequate operational data to provide the basis for future commercial activities, including hydrogen fueling stations.

Technical Barriers

This project addresses the following technical barriers from the Technology Validation section (3.5.4) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (C) Hydrogen Refueling Infrastructure
- (I) Hydrogen and Electricity Co-production

Contribution to Achievement of DOE Technology Validation Milestones

This project will contribute to achievement of the following DOE Technology Validation milestones from the Technology Validation section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- **Milestone 37:** Demonstrate prototype energy station for 6 months; projected durability >20,000 hours; electrical energy efficiency >40%; availability >0.80. (4Q, 2008)
- **Milestone 38:** Validate prototype energy station for 12 months; projected durability >40,000 hours; electrical energy efficiency >40%; availability >0.85. (1Q, 2014)

Accomplishments

- Completed installation of fuel cell and anode exhaust skid for shop validation test at FuelCell Energy's facility in Danbury, CT, and completed >4,000 hours of integrated operation.
- Completed fabrication and installation of hydrogen purification equipment at FuelCell Energy.
- Completed commissioning and start-up of hydrogen energy station equipment and full integration of fuel cell with hydrogen purification system.
- Successfully demonstrated >84 hours of unattended hydrogen production.
- Air Products executed a grant agreement with California Air Resources Board to support the existing DOE project and to add a new 100 kilogram per day fueling station to provide renewable hydrogen to fuel cell vehicles; the system will be installed and operated for three years at Orange County Sanitation District in Fountain Valley, CA. The board of South Coast Air Quality Management District has also approved funding into the project.

Introduction

One of the immediate challenges in the development of hydrogen as a transportation fuel is finding the optimal means to roll out a hydrogen-fueling infrastructure concurrent with the deployment of hydrogen vehicles. The low-volume hydrogen requirements in the early years of fuel cell vehicle deployment make the economic viability of stand-alone, distributed hydrogen generators challenging. A potential solution to this “stranded asset” problem is the use of hydrogen energy stations that produce electricity in addition to hydrogen. To validate this hypothesis, a four-phase project is being undertaken to design, fabricate and demonstrate a high-temperature fuel cell co-production concept. The basis of the demonstration will be a FuelCell Energy DFC®-300 molten carbonate fuel cell modified to allow for the recovery and purification of hydrogen from the fuel cell anode exhaust using an Air Products-designed hydrogen purification system.

The DFC® technology is based on internal reforming of hydrocarbon fuels inside the fuel cell, integrating the synergistic benefits of the endothermic reforming reaction with the exothermic fuel cell reaction. The internal reforming of methane is driven by the heat generated in the fuel cell and simultaneously provides efficient cooling of the stack, which is needed for continuous operation. The steam produced in the anode reaction helps to drive the reforming reaction forward. The hydrogen produced in the reforming reaction is used directly in the anode reaction, which further enhances the reforming reaction. Overall, the synergistic reformer-fuel cell integration leads to high (~50%) electrical efficiency.

The baseline electric DFC® is designed to operate at 75% fuel utilization in the stack. The remaining 25% of fuel from the anode presents a unique opportunity for low-cost hydrogen, if it can be recovered from the dilute anode effluent gases. The recovery and purification of hydrogen from the anode presents several challenges:

1. The anode off-gas is a low-pressure, high-temperature gas stream that contains ~10% hydrogen by volume.
2. The anode exhaust stream must be heat integrated with the fuel cell to ensure high overall system efficiency.
3. The parasitic power used for purification must be optimized with the hydrogen recovery and capital cost to enable an economically viable solution.

Approach

A hydrogen energy station that uses a high-temperature fuel cell to co-produce electricity and

hydrogen will be evaluated and demonstrated in a four-phase project. In Phase 1, Air Products completed a feasibility study on the technical and economic potential of high-temperature fuel cells for distributed hydrogen and power generation. As part of the Phase 1 analysis, three different high-temperature fuel cells were evaluated to determine the technology most suitable for a near-term demonstration. FuelCell Energy's DFC®-300 technology was selected for concept development. In Phase 2, a process design and cost estimate were completed for the hydrogen energy station that integrates the high-temperature fuel cell with a pressure-swing adsorption (PSA) system selected and designed by Air Products. Economics were developed based on actual equipment, fabrication, and installation quotes as well as new operating cost estimates. High-level risks were identified and addressed by critical component testing. In Phase 3, a detailed design for the co-production system was initiated. The system will be fabricated and shop tested. Prior to shipping to the field, the entire system will be installed at FuelCell Energy's facility in Danbury, CT for complete system check-out and validation. In Phase 4, the system will be operated for a desired period of 6 months. Data from the operations phase will be used to validate the system versus DOE and economic performance targets.

Results

Figure 1 shows the process flow diagram for the hydrogen energy station. Methane (in this case, from natural gas) is internally reformed at the fuel cell anode to hydrogen and carbon dioxide. The fuel cell operates near 600°C and uses molten carbonate electrolyte as the charge carrier. Heated air is combined with the waste gas from the hydrogen purification system and oxidized. These waste gases are fed to the cathode. The fuel cell cathode converts waste gas carbon dioxide to the carbonate charge carrier to complete the fuel cell circuit. The fuel cell stack generates a direct current voltage, which is then converted to alternating current (AC) by an inverter in the electrical balance of plant (E-BOP). The system produces 480 VAC, 60 HZ, and a nominal 300 kW without hydrogen production. Excess carbon dioxide and water leave the cathode as exhaust, and heat can be recovered from these exhaust gases.

About 70 to 80% of the hydrogen is converted to power, and some hydrogen remains available for recovery. The anode exhaust gas is cooled and sent to a water-gas shift catalytic reactor to convert most of the carbon monoxide present in the stream to hydrogen and carbon dioxide. After an additional cooling step, this gas stream is then compressed and sent to the PSA system. The PSA uses adsorbents to remove carbon monoxide, carbon dioxide, and water to produce a high-purity hydrogen stream. The waste gas from the PSA is catalytically oxidized and returned to the cathode. The

FIGURE 1. Hydrogen Energy Station Process Flow Diagram

PSA system can also be placed in stand-by mode to stop hydrogen production and allow for maximum power production by the DFC® system, thereby improving the system efficiency and economics.

In late 2008, the hydrogen energy station was installed at FuelCell Energy's facilities in Danbury, CT for a system check-out and validation of performance on natural gas. A photograph of the DFC®300 is provided in Figure 2, and a photograph of the anode exhaust processing and hydrogen purification system is provided in Figure 3.

The hydrogen-ready DFC®300 fuel cell was installed and brought onstream first, and stable operation at varying loads up to 200 kW-net AC was achieved. Procedures were developed for startup, shutdown and upset conditions during this operability test. The fuel cell was then integrated with the anode exhaust gas system, which includes the water-gas shift reactors and gas cooling systems. The hydrogen purification system was bypassed during this period to integrate this equipment with the fuel cell. During testing, the content of carbon monoxide exiting the reactors achieved the design target of less than 0.5 vol%, and hydrogen concentration was increased from 18 vol% to 29 vol%.

FIGURE 2. Hydrogen-Ready DFC®-300 Fuel Cell

FIGURE 3. Hydrogen Energy Station Anode Exhaust and Hydrogen Purification Systems

The final step of the shop validation test was in the integration of the hydrogen purification equipment. The technical challenges during this operation are (1) the minimization of pressure fluctuations during the return of tail gas from the PSA system and (2) the need for continuous flow of CO₂-containing gas to the cathode of the fuel cell in order to maintain the continuity of the electrical circuit. Through mid-March 2009, the hydrogen energy station has been operated at 50% electrical load, and purified hydrogen has been produced from the PSA system.

Air Products was selected under California Air Resources Board Solicitation 06-618, “Establish Demonstration Hydrogen Refueling Stations,” to install a renewable-based hydrogen fueling station and cleanup system for anaerobic digester gas at Orange County Sanitation District (OCSD) in Fountain Valley, CA. Hydrogen will be produced utilizing the hydrogen energy station. Figure 4 shows the integration of the hydrogen energy station with the existing water treatment facility at OCSD. The hydrogen fueling station (sized at 100 kilograms per day) and a gas cleanup skid to remove contaminant species such as sulfur from the anaerobic digester gas supply will be installed under a second DOE project (Cooperative Agreement No. DE-FC36-05GO85026).

Conclusions and Future Direction

Planned future work includes:

- Complete the shop validation test of the hydrogen energy station. Additional operation on natural gas will be performed to generate data at higher production rates and to automate the integration and de-integration of the hydrogen purification

system from the fuel cell. Testing on a simulated digester gas stream will also be performed to obtain baseline performance.

- Ship the hydrogen energy station to OCSD. Operation will begin on natural gas to compare performance with the results of the shop validation test. Digester gas will then be introduced to the system to demonstrate the production of renewable electricity and hydrogen and to supply the hydrogen fueling station.
- The current DOE project includes operation of the hydrogen energy station for up to 6 months.

FY 2009 Publications/Presentations

1. Presentation at the “Future is Green” Conference sponsored by the California Air Pollution Control Officers Association, Long Beach, CA, September 2008.
2. Presentation at National Hydrogen Association Fall Forum on Renewable Hydrogen, Golden, CO, September 2008.
3. Presentation at Fuel Cell Seminar 2008, Phoenix, AZ, October 2008.
4. Panel presentation at DOE-EERE Workshop on Integration of Stationary Fuel Cells in Transportation Fuel Cell Applications, Phoenix, AZ, October 2008.
5. Presentation at National Hydrogen Association 2009 Conference, Columbia, SC, April 2009.
6. Presentation at the DOE Annual Merit Review Meeting, Arlington, VA, May 2009.
7. Presentation at Canadian Hydrogen Fuel Cell Conference 2009, Vancouver, CN, June 2009.
8. Presentation at DOE Trigenation Workshop at UC Irvine and ASME International Conference, Newport Beach, CA, June 2009.

FIGURE 4. Hydrogen Energy Station Demonstration at Orange County Sanitation District

VIII.7 California Hydrogen Infrastructure Project

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Contract Number: DE-FC36-05GO85026

Working Partners/Subcontractors:

- University of California, Irvine (UCI)
- National Fuel Cell Research Center (NFCRC)

Project Start Date: August 1, 2005

Project End Date: December 31, 2010

Contribution to Achievement of DOE Technology Validation Milestones

This project will contribute to achievement of the following DOE technology validation milestones from the Technology Validation section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- **Milestone 23:** Total of 10 stations constructed with advanced sensor systems and operating procedures. (1Q, 2008).

Accomplishments

- Continued operation of permanent station (350 and 700 bar gaseous hydrogen) opened at UCI.
- Completed deployment of mobile station (HF-150) operational in Long Beach, CA.
- Deployment of NDC trailer.
- Continued development of hydrogen pipeline fueling station in Torrance, CA.

Objectives

- Demonstrate a cost-effective infrastructure model in California for possible nationwide implementation:
 - Design, construct and operate seven hydrogen fueling stations.
 - Collect and report infrastructure data.
 - Document permitting requirements and experiences.
 - Validate expected performance, cost, reliability, maintenance, and environmental impacts.
- Implement a variety of new technologies with the objective of lowering costs of delivered H₂:
 - New Delivery Concept (NDC).
 - High-pressure/high-purity clean-up equipment.

Technical Barriers

This project addresses the following technical barriers from the Technology Validation section (3.6.4) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

(C) Hydrogen Refueling Infrastructure

Introduction

Air Products and Chemicals, Inc. is leading a comprehensive, multiyear project to demonstrate a hydrogen infrastructure in California. The specific primary objective of the project is to demonstrate a model of a “real-world” retail hydrogen infrastructure and acquire sufficient data within the project to assess the feasibility of achieving the nation’s hydrogen infrastructure goals. The project will help to advance hydrogen station technology, including the vehicle-to-station fueling interface, through consumer experiences and feedback. By encompassing a variety of fuel cell vehicles, customer profiles and fueling experiences, this project is obtaining a complete portrait of *real market needs*. The project is also opening its stations to other qualified vehicle providers at the appropriate time to promote widespread use and gain even broader public understanding of a hydrogen infrastructure. The project is engaging major energy companies to provide a fueling experience similar to traditional gasoline station sites to foster public acceptance of hydrogen.

Approach

Work over the course of the project was focused in multiple areas. With respect to the equipment needed, technical design specifications were written, reviewed, and finalized. Both safety and operational

considerations were a part of this review. After finalizing individual equipment designs, complete station designs were started including process flow diagrams and systems safety reviews. Material quotes were obtained, and in some cases, depending on the project status and the lead time, equipment was placed on order and fabrication was started. Consideration was given for expected vehicle usage and station capacity, standard features needed, and the ability to upgrade the station at a later date.

In parallel with work on the equipment, discussions were started with various vehicle manufacturers to identify vehicle demand (short and long term needs). Discussions included identifying potential areas most suited for hydrogen fueling stations, with focus on safe, convenient, fast-fills. These potential areas were then compared and overlaid with suitable sites from various energy companies and other potential station operators. Work continues to match vehicle needs with suitable fueling station locations. Once a specific site has been identified, the necessary agreements can be completed with the station operator and expected station users.

Detailed work can begin on the site drawings, permits, safety procedures and training needs. Once stations are brought online, infrastructure data will be collected and reported to DOE using Air Products' enterprise remote access monitoring system. Feedback from station operators will be incorporated to improve the station user's fueling experience.

Results

The first of the hydrogen fueling stations within the California Hydrogen Infrastructure Project continued operation at the NFCRC at UCI. The capability for fueling vehicles with gaseous hydrogen at 350 bar, involving the installation of a 1,500 gallon horizontal liquid hydrogen tank, 2 kg/hr compressor skid, storage for 50 kg of hydrogen, and a dual dispenser for both 350 and 700 bar hydrogen was brought onstream in August of 2006. The 700 bar system, including the installation of a booster compressor, was commissioned in February of 2007. Based on a 50% compressor on-stream factor, the station has the capacity to dispense 24 kg/day or approximately 6 cars per day. When starting with full storage, 4-5 cars can be filled in succession. The station continues to see increasing use over time, with operation exceeding 75% of rated capacity on most days as additional hydrogen-fueled vehicles are being deployed in the Irvine area. A photograph of the dispensing system is provided in Figure 1.

The HF-150 (shown in Figure 2) is ideal for small fleet fueling and offers the advantages of being a highly reliable, cost-effective, and automated fueling system that can be easily installed. The HF-150 maintains about 150 kg of gaseous hydrogen at 6,600 psig. It can

FIGURE 1. UCI 350/700 Bar Gaseous Hydrogen Dispenser

FIGURE 2. Air Products HF-150 Hydrogen Fueler

dispense approximately 80 to 90 kg before needing to be refilled. Air Products completed the deployment of an HF-150 mobile fueler at the facilities of Long Beach Gas & Oil at 2400 E. Spring Street. Discussions continued regarding a second HF-150 deployment with the U.S. Forest Service in Placerville, CA.

The world's first fueling station supplied by a hydrogen pipeline is being developed to demonstrate a low-cost, reliable supply of hydrogen. A site in the Torrance, CA area in proximity to an existing Air Products hydrogen pipeline is being considered. A 4 kg/hr compressor skid and a total of 50 kg of high-pressure hydrogen storage are being provided. Hydrogen purification technology will be deployed for the first time in this application to demonstrate the production of an ultra-pure hydrogen stream from the industrial-grade pipeline supply. A dual dispenser for both 350 and 700 bar hydrogen is being provided. Based on a 50% compressor on-stream factor, the station will have the capacity to dispense 48 kg/day or approximately 12 cars per day. When starting with full storage, six cars can be filled in succession. The design of the station is intended

to provide the ability to double storage capacity in the future. The agreement with the station operator has been executed, and detailed mechanical and electrical designs have been completed. The station operator has begun the process to secure the necessary permits to allow for station construction to commence.

The NDC trailer is a new method of hydrogen distribution capable of supplying low-, medium-, and high-pressure systems using a single liquid hydrogen trailer (Figure 3). The NDC trailer provides a tenfold increase in the amount of transported hydrogen compared with traditional tube trailers. This delivery system can be utilized to supply existing merchant bulk hydrogen and liquid hydrogen supply chains as well as hydrogen fueling stations, resulting in greater equipment utilization. Delivery pressures as high as 8,000 psig are achieved, and no utilities are required from the receiving stations. The trailer was deployed to California in April 2008.

FIGURE 3. Air Products NDC Trailer

Air Products was selected under California Air Resources Board Solicitation 06-618, “Establish Demonstration Hydrogen Refueling Stations,” to install a renewable-based hydrogen fueling station and cleanup system for anaerobic digester gas at Orange County Sanitation District (OCSD) in Fountain Valley, CA. Hydrogen will be produced utilizing the Hydrogen Energy Station concept being developed under a second DOE project (Cooperative Agreement No. DE-FC36-01GO11087). Figure 4 shows the integration of the hydrogen energy station with the existing water treatment facility at OCSD. Modifications to the Cooperative Agreement are being developed to include a no-cost time extension and to modify the statement of work for the procurement and installation of a hydrogen fueling station (sized at 100 kilograms per day) and of a gas cleanup skid to remove contaminant species such as sulfur from the anaerobic digester gas that will be fed to the hydrogen energy station.

Conclusions and Future Directions

Planned future work includes:

- UCI Fueling Station – continue operation of gaseous dispensers.
- Torrance Pipeline Fueling Station – Following approval of permits, install and commission both 350 and 700 bar systems.
- Fountain Valley Renewable Station – Acquire necessary permits, install and commission both 350 and 700 bar systems.
- Hydrogen Fuelers (HF-150) – Work to finalize second deployment in northern California.
- Infrastructure data acquisition, analysis and delivery – report data to DOE.

FIGURE 4. Fountain Valley Renewable Hydrogen Station Flow Diagram

FY 2009 Publications/Presentations

1. A presentation regarding the overall project status was given at the DOE Annual Merit Review Meeting (May 2009).

VIII.8 Technology Validation: Fuel Cell Bus Evaluations

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Kevin Chandler, Battelle, Columbus, OH

Start Date: March 2001

Projected End Date: Projected continuation
and direction determined annually by DOE

natural gas (CNG) vehicles. Results for these first-generation evaluations have shown:

- Non-hybrid FCBs have a 12% lower fuel economy compared to diesel buses.
- Hybrid FCBs have demonstrated a 71% higher fuel economy compared to diesel buses and a 141% higher fuel economy compared to CNG buses.

- **Milestone 8: Fuel cell vehicles demonstrate the ability to achieve a 250-mile range without impacting the passenger cargo compartment.** Based on in-service fuel economies between 5 and 7 miles per kilogram, hybrid FCBs can achieve a range between 250 and 350 miles per fill. This efficiency depends on duty-cycle. There are no major issues with lost cargo/passenger space on transit buses because the tanks are typically mounted on the roof; however, the added weight of the system limits the number of standing passengers allowed on the buses.

Objectives

- Determine the status of fuel cell bus (FCB) technologies in transit applications by evaluating them in real-world service.
- Coordinate with the Federal Transit Administration (FTA) on the data collection for the National Fuel Cell Bus Program and international work groups to harmonize data-collection methods and enable the comparison of a wider set of vehicles.

Technical Barriers

This project addresses the following technical barriers from the Technology Validation section of the Hydrogen, Fuel Cells & Infrastructure Technologies Program Multi-Year Research, Development, and Demonstration Plan:

- (A) Lack of Fuel Cell Vehicle Performance and Durability Data
- (C) Lack of H₂ Fueling Infrastructure Performance and Availability Data
- (D) Maintenance and Training Facilities

Contribution to Achievement of DOE Technology Validation Technical Targets

- **Milestone 2: Demonstrate fuel cell vehicles that achieve 50% higher fuel economy than gasoline vehicles.** We are comparing nine heavy-duty, first-generation fuel cell vehicles of various configurations to baseline diesel or compressed

Accomplishments

- Collected, analyzed, and reported up to 27 months of performance and operational data on five full-size hybrid FCBs in revenue service in the United States.
- Began data collection on next-generation fuel cell system in revenue service.

Introduction

The transit industry has become an excellent “test-bed” for developing and optimizing advanced transportation technologies. Demonstrations of FCBs are being conducted in transit organizations all over the world. Although progress has been made, more work is needed to improve reliability and durability of fuel cell systems to meet the needs of transit agencies.

Demonstration programs are necessary to validate the performance of the current generation of fuel cell systems. Lessons learned will help assess the status of FCB technology and determine issues that require further development. Early prototype FCBs have demonstrated improved performance characteristics – faster acceleration, lower noise, and no tailpipe emissions – over conventional buses in transit applications. We need to surmount barriers to the use of fuel cells in transportation applications, however, before these technologies can be commercialized. Future evaluations should help address these barriers,

which include extending the life of fuel cells, improving reliability and durability of the systems, and lowering vehicle and infrastructure costs.

Approach

Researchers at the National Renewable Energy Laboratory (NREL) and Battelle have developed an evaluation protocol to provide:

- Comprehensive, unbiased evaluation results of advanced technology vehicle development and operations.
- Evaluations of hydrogen infrastructure development and operation.
- Descriptions of facility modifications required for the safe operation of FCBs.
- Detailed results on fuel cell systems for buses and the requisite hydrogen infrastructure to complement the light-duty demonstrations and further DOE goals.

The evaluation protocol includes two levels of data: operation and maintenance data on the bus and infrastructure, and more detailed data on the fuel cell, system, and components. The first set of data is considered non-sensitive and is obtained mainly from the transit fleet. The analysis, which consists of economic, technical, and safety factors, focuses on performance and use, including progress over time and experience with vehicle systems and supporting infrastructure.

The detailed data are collected with cooperation from the bus/fuel cell system manufacturers and are considered highly sensitive. Results will include aggregate data products that protect each manufacturer's specific data. NREL has begun to collect this data and will publish aggregate results when enough data are available.

Results

Bus Evaluations

During Fiscal Year 2009, NREL collected data from three FCB demonstrations in the United States:

- Alameda-Contra Costa Transit District (AC Transit) in Oakland, CA.
- SunLine Transit Agency in Thousand Palms, CA
- Connecticut Transit (CTTRANSIT) in Hartford, CT

NREL has published detailed reports on all three demonstrations. A summary of selected results from each project follows.

AC Transit

AC Transit has operated its three FCBs since March 2006. The FCBs were manufactured by Van Hool and ISE Corp. They feature electric-hybrid drive systems with UTC Power fuel cell power systems and ZEBRA batteries for energy storage. The agency procured the buses to meet the demonstration requirements under the California Air Resources Board Transit Bus Fleet Rules. (Note: The FCBs at SunLine and CTTRANSIT were included in this procurement and are essentially identical to the buses at AC Transit.)

NREL collected operational and performance data on these buses in comparison to six similar Van Hool diesel buses in the same operation. Three reports outlining the early experience and data results were published in 2007 and 2008. The third report (July 2008) completed the evaluation of the first-generation FCBs at AC Transit planned under DOE funding. NREL has continued to evaluate these buses with new fuel cell systems under FTA funding. The data presented in this report include the more recent data under the FTA program. AC Transit has ordered 12 more next-generation FCBs to be delivered in fall 2009. These buses will be evaluated under DOE funding (if available). Table 1 summarizes a selection of the most recent results.

TABLE 1. Summary Data Results on AC Transit

	FCB	Diesel
Number of buses	3	6
Data period	~11/07 – 10/08	1/07-12/07
Total fleet miles	49,600	266,514
Average miles per month	1,837	3,702
Total fuel cell hours	4,957	—
Fuel economy (mi./diesel equivalent gal)	7.33	4.2
Average speed (mph)	10.1	not available
Availability	61%	85%
Fueling cost (\$/mi.)	1.23	0.55

AC Transit began operating its three FCBs in March 2006. At that time, the agency scheduled two buses for weekday service with the third kept as a spare to allow for maintenance, training, and special events. In November 2007, AC Transit began accelerated testing of the buses under the FTA's National Fuel Cell Bus Program. At that time, UTC Power installed new fuel cell systems in the buses that were expected to perform much better with respect to the number of operating hours than the previous version. To test this, AC Transit began operating each bus for up to 16 hours per day including some weekend service. During the evaluation period, the

FCBs operated more than 49,000 miles and accumulated nearly 5,000 total fuel cell system hours.

The overall availability of the buses has generally been lower than AC Transit's fleet goal of 85%. This lower availability has primarily been because of issues with the traction batteries. The issues include problems with matching the state-of-charge (SOC) among the three traction batteries, the software to manage this SOC, and the interface between the propulsion system software and traction battery software. The manufacturers continue to work on these issues to support maximum operation of the FCBs; however, it continues to be the major obstacle to the accelerated testing activity.

Monthly average fuel economy for the FCBs is shown in Figure 1. The FCBs averaged 6.49 miles per kg of hydrogen for the evaluation period, which equates to 7.33 miles per diesel gallon equivalent. The average fuel consumption for the diesel buses was 4.2 mpg, which indicates that the FCBs have an average fuel economy 75% higher than the diesel buses.

The operating cost for hydrogen production and dispensing for AC Transit is currently estimated at \$8 per kg. This excludes capital expenses and was generated using early data (not optimized operation) and conservative maintenance and operating estimates. This equates to a cost for the FCBs of \$1.23 per mile. The average diesel fuel cost per gallon during the evaluation period was \$2.29 per gallon, which equates to a cost of \$0.55 per mile.

SunLine Transit Agency

SunLine has been operating one prototype FCB in service since January 2006. The FCB is essentially the same as the buses at AC Transit. NREL collected operational and performance data on the bus in comparison to five new CNG buses in the same operation. Three reports have been published outlining the early experience and data results from the first

generation fuel cell system. In April 2008, a new version fuel cell system was installed. A fourth report was published in early 2009 that outlined the data results on the new fuel cell system. Table 2 summarizes a selection of the results.

TABLE 2. Summary Data Results on SunLine

	FCB	CNG
Number of buses	1	5
Data period	4/08 – 10/08	
Total fleet miles	11,461	159,150
Average miles per month	1,694	4,547
Total fuel cell hours	885	--
Fuel economy (mi./diesel equivalent gal)	8.19	3.16
Average speed (mph)	13	13.2
Availability	76%	86%
Fueling cost (\$/mi.)	1.10	0.61

Since the installation of the new fuel cell system through October 2008, SunLine operated the FCB more than 11,000 miles. Using the CNG buses as the baseline, the FCB's average monthly mileage was about one third that of the CNG operation.

Figure 2 shows the average monthly fuel economies for each of the study groups of buses. The average fuel economy for the FCB was fairly constant during this time frame. Using the CNG buses as the baseline, the FCBs had a fuel economy more than 2.5 times higher than the CNG buses. SunLine estimates that the best steady-state operating point for its reformer would result in an average hydrogen cost of around \$8 per kilogram. (Actual cost varies based on current natural gas cost and station load.) SunLine paid \$1.72 per gasoline gallon equivalent for CNG during the data-collection period.

FIGURE 1. Monthly Fuel Economy (diesel equivalent), AC Transit

FIGURE 2. Monthly Fuel Economy (diesel equivalent), SunLine

The fuel costs per mile were \$1.10 for the FCB and \$0.61 for the CNG buses.

SunLine has an availability goal of 85% for all buses. The CNG buses exceeded this goal at 86% availability. The FCB achieved an availability of 76% during this time period. The FCB was available at or near the target six out of the seven months including two months at 100% availability. This is an improvement over what was previously reported (66%).

CTTRANSIT

CTTRANSIT began operating its FCB in revenue service beginning in March 2007. The FCB is essentially the same system as the buses at AC Transit and SunLine. This demonstration site is the first cold-weather location for the bus.

NREL collected operational and performance data on the bus in comparison to three of CTTRANSIT's newest diesel buses, which are 40-foot New Flyer buses. The FCB is currently being operated on a downtown circulator route, which involves low-speed, stop-and-go driving. The diesel buses are operated on all of CTTRANSIT's routes, which results in a faster average speed. Table 3 summarizes a selection of the results.

TABLE 3. Summary Data Results on CTTRANSIT

	FCB	Diesel
Number of buses	1	3
Data period	1/08 – 2/09	
Total fleet miles	24,127	137,127
Average miles per month	1,723	3,265
Total fuel cell hours	3,544	—
Fuel economy (mi./diesel equivalent gal)	5.34	3.66
Average speed (mph)	6.8	12
Availability	77%	85%
Fueling cost (\$/mi.)	1.12	0.74

CTTRANSIT has operated its FCB since April 2007. In January 2008 the bus had a new version fuel cell system installed, similar to that of the other two agencies. At that time, CTTRANSIT began accelerated operation of the bus, scheduling service for two shifts per day and some weekend service. During the evaluation period, the FCB operated 24,127 miles and accumulated 3,544 fuel cell system hours. Overall availability for the FCB was 77%, which is an improvement from what was previously reported (53%). CTTRANSIT's goal for availability for their fleet is 85%.

Monthly average fuel economy for the FCBs and diesel buses is shown in Figure 3. The FCB averaged

FIGURE 3. Monthly Fuel Economy (diesel equivalent), CTTRANSIT

4.7 miles per kg of hydrogen for the evaluation period, which equates to 5.3 miles per diesel gallon equivalent. The diesel buses averaged 3.66 mpg. Using the diesel buses as a baseline, the FCB has an average fuel economy 46% higher.

CTTRANSIT fuels its FCB at the UTC Power hydrogen station. The cost for hydrogen for CTTRANSIT is currently \$5.29 per kg. This equates to a cost for the FCBs of \$1.12 per mile. The average diesel fuel cost per gallon during the evaluation period was \$2.70 per gallon, which equates to a fueling cost of \$0.74 per mile.

The fuel economy for transit buses is highly dependent on the duty-cycle. Figure 4 illustrates this by comparing each fleet result side-by-side. The same design FCB achieves different results under varied conditions. This bus gets the lowest fuel economy in the low speed (6.8 mph average speed), high idle time, and stop-and-go duty cycle at CTTRANSIT. The bus in service at SunLine achieves the highest fuel economy, where the duty cycle includes high speed (14 mph average speed) with long distances between stops and little idle time.

FTA Data Collection/International Coordination

FTA has funded NREL to evaluate each of the demonstrations under its National Fuel Cell Bus Program. The evaluations follow the same protocol as the DOE-funded evaluations. This will provide similar data and analysis on a wider array of fuel cell systems in buses, which will aid in determining the progress of the technology toward market readiness. Through the FTA funding NREL also continues to work with international groups to collaborate among FCB demonstrations worldwide. A core group of agencies – NREL, FTA, the Electric Drive Transportation Association, and the Northeast Advanced Vehicle Consortium – coordinated the 6th International Fuel Cell Bus Workshop in Vancouver, Canada, in June 2009.

FIGURE 4. Fuel Economy Comparison by Fleet (diesel equivalent)

Conclusions and Future Directions

First-generation fuel cell propulsion systems in buses are showing progress, although they are considered prototypes in the early stages of technological development. Manufacturers have learned from the results of these first-generation demonstrations and are incorporating design improvements into the next-generation systems. There are still challenges to overcome, and more data are needed on these new systems just being introduced. Remaining challenges include:

- Costs of purchasing, operating, and maintaining buses and infrastructure.
- Durability/reliability of the fuel cell systems and other components.
- Fully trained transit personnel to maintain all aspects of the buses.

Future work includes:

- Collecting, analyzing, and reporting on performance data for next-generation hydrogen-fueled vehicles in service at the following sites:
 - Bay Area FCB Demonstration led by AC Transit
 - Connecticut Transit
 - City of Burbank
 - Additional sites as funding allows
- Investigating reliability, durability, and life cycle of FCBs as a part of ongoing evaluations; these efforts complement the DOE light-duty fuel cell vehicle demonstrations.
- Coordinate with FTA to ensure harmonized data-collection efforts for the National Fuel Cell Bus Program.
- Coordinate with FTA to plan the 7th International Fuel Cell Bus Workshop in 2010.

FY 2009 Publications/Presentations

1. Chandler, K., Eudy, L. (2008). *Alameda-Contra Costa Transit District, Fuel Cell Transit Buses: Third Evaluation Report and Appendices*, NREL/TP-540-43545-1 & NREL/TP-540-43545-2, NREL, Golden, CO, July.
2. Eudy, L., Chandler, K. (2008). *NREL Technology Validation: Results for FCB Evaluations*. Presentation for the APTA Bus Technical, Maintenance, & Procurement Workshop and EXPO, San Diego, CA, Oct.
3. Eudy, L. (2008). *Fuel Cell Bus Evaluation Results*. Presentation for the 2008 Fuel Cell Seminar, Phoenix, AZ, Oct.
4. Eudy, L. (2008). *CTTRANSIT, Fuel Cell Transit Bus: Preliminary Evaluation Results*. NREL/TP-560-43847, NREL, Golden, CO, Oct.
5. Eudy, L. (2008). *Fuel Cell Buses in U.S. Transit Fleets: Current Status 2008*. Presentation for the 2008 California Transit Association Conference, Monterey, CA, Nov.
6. Eudy, L., Chandler, K., Gikakis, C. (2008). *Fuel Cell Buses in U.S. Transit Fleets: Current Status 2008*. NREL/TP-560-44133, NREL, Golden, CO, Dec.
7. Eudy, L. DOE/NREL (2009). *Fuel Cell Bus Evaluation Results*. Presented at the 88th Annual Transportation Research Board Meeting, Washington, D.C., Jan.
8. Chandler, K., Eudy, L. (2009). *SunLine Transit Agency, Fuel Cell Transit Bus: Fourth Evaluation Report and Appendices*. NREL/TP-560-44646-1, and NREL/TP-560-44646-2, NREL, Golden, CO, Jan.
9. Eudy, L. (2009). *CTTRANSIT, Fuel Cell Transit Bus: Second Evaluation Report and Appendices*. NREL/TP-560-45670-1 & NREL/TP-560-46570-2, NREL, Golden, CO, May.
10. Eudy, L. (2009). *Technology Validation: Fuel Cell Bus Evaluations*. Presented at the 2009 Annual Merit Review, Arlington, VA, May.

VIII.9 Hawaii Hydrogen Center for Development and Deployment of Distributed Energy Systems

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Contract Number: DE-FC51-02R021399 A008

Partners:

- State of Hawaii Department of Business, Economic Development & Tourism, Honolulu, HI
- Volcanoes National Park
- Kilauea Military Camp
- Hawaii Center for Advanced Transportation Technologies
- Hawaiian Electric Company, Honolulu, HI
- Hawaii Electric Light Company, Hilo, HI
- Sandia National Laboratories, Albuquerque, NM
- National Renewable Energy Laboratory (NREL)
- Puna Geothermal Ventures
- Office of Naval Research

Project Start Date: June 29, 2009
Project End Date: September 30, 2012

Objectives

- Install hydrogen fueling station infrastructure at Hawaii Volcanoes National Park (HAVO) on the Big Island of Hawaii;
- Support the operations of the National Park Service (NPS) hydrogen plug-in hybrid electric vehicle (PHEV) shuttle buses for 24 months through January 2012;
- Conduct engineering and economic analysis of HAVO bus operations on different routes, grades, elevations and climatic conditions;
- Validate fuel cell system performance in harsh environments including high SO₂ concentrations;
- Position HAVO as an alternative-fueled vehicle test bed for the NPS;

- Attract new partners and applications for the Big Island hydrogen infrastructure; and
- Conduct outreach to local authorities and the general public regarding hydrogen infrastructure.

Technical Barriers

This project addresses the following technical barriers from the indicated sections of the April 2009 edition of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

Technology Validation, Section 3.6.4

- (A) Lack of Fuel Cell Vehicle Performance and Durability Data
- (C) Lack of Hydrogen Refueling Infrastructure Performance and Availability Data
- (H) Hydrogen from Renewable Resources

Hydrogen Safety, Section 3.8.4

- (H) Lack of Hydrogen Knowledge by Authorities Having Jurisdiction

Contribution to Achievement of DOE Technology Validation Milestones

This project will contribute to the following DOE milestones from sections of the Multi-Year Research, Development and Demonstration Plan:

Technology Validation section 3.6.6 Milestones

- **Milestone 34: Complete power park demonstrations and make recommendations for business case economics. (2Q, 2008)** Our HAVO system will generate hydrogen utilizing an electrolyzer powered by renewable energy resources delivered over the grid. Data will be collected to evaluate cost and technical performance.

Approach

- Procure a turn-key H₂ fueling station designed for easy expansion;
- Use fuel cell PHEVs to maximize the efficiency of a new park shuttle bus service at HAVO;

- Collaborate with existing data analysis groups (Sandia and NREL) to compare system data under different operating conditions (fueling station and vehicles);
- Evaluate the effect of different grades, climatic zones, and air quality conditions including SO₂ on vehicle performance;
- Identify areas that require further technical development such as air filtration systems; and
- Transfer results to industry and government agencies.

Accomplishments

- Signed an implementation agreement with the State of Hawaii contracting Hawaii Natural Energy Institute as the project “Implementing Partner” on behalf of the State of Hawaii;
- Secured State of Hawaii \$1.2 million cost share funds via Kolohala Holdings LLP;
- Completed a hydrogen station specification;
- Issued an request for proposal for the supply of “turn-key” fueling station. Responses are due on August 14th, 2009;
- Applied for a special research and development energy supply agreements from the Hawaiian Electric Light Company through the State of Hawaii Public Utilities Commission;
- Obtained Kilauea Military Camp (KMC) approval and support as the site of the fueling station;
- Progressed permitting and National Environmental Policy Act documentation;
- Completed background noise survey at the KMC site;
- Assisted HAVO to develop a noise specification for the fueling station; and
- Assisted HAVO to secure bus funding (\$1 million).

Future Directions

- Select the supplier for fueling station – September 2009.
- Complete site prep for station – Fall 2009.
- Install the fueling station – target: April 2010 or sooner.
- Complete vehicle conversions – target: April 2010. (Note: This is a related HAVO project and not part of the Power Park funding.)
- Operate buses – April 2010 to March 2012.
- Collect and analyze fueling station and vehicle data.
- Seek opportunities for expansion of fleet and/or additional hydrogen infrastructure.

FY 2009 Publications/Presentations

1. M. Ewan and R. Rocheleau, “The Hawaii Renewable Hydrogen Program,” *National Hydrogen Association Conference & Expo*, Columbia, South Carolina. March 2009.
2. R. Rocheleau and M. Ewan, “The Hawaii Hydrogen Power Park,” *US DOE Annual Merit Review*, Washington, D.C., May 2009.

VIII.10 Detroit Commuter Hydrogen Project*

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Contract Number: DE-FG36-06GO86051

Project Start Date: January 21, 2009

Project End Date: August 30, 2010

*Congressionally directed project

Objectives

- To evaluate the feasibility of using renewable fuels as a part of a sustainable transportation infrastructure, feeding a regional, public mass-transit system.
- To compare reliability, acceptability and cost effectiveness of hydrogen and propane/gasoline internal combustion engine powered buses.

Technical Barriers

This project addresses the following technical barriers from the Technology Validation section (3.6.4) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) Lack of Vehicle Performance and Durability Data
- (B) Hydrogen Storage
- (C) Lack of Hydrogen Fueling Infrastructure Performance and Availability Data

Contribution to Achievement of DOE Technology Validation Milestones

This project will contribute to achievement of the following DOE milestones from the Technology Validation milestone section 3.6.6 of the Hydrogen, Fuel

Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- **Milestone 5: Validate vehicle refueling time of 5 minutes or less for a 5 kg tank (1 kg/min). (4Q, 2006)**
The buses in the Detroit Commuter Hydrogen project are hydrogen-fueled internal combustion engine buses (H2ICE). They have been able to demonstrate some fuel fill times that meet the 1 kg/min target. Filling the 30 kg tanks of the buses has been done in some cases with rates as high as 1.4 kg/min. However, average fill rates have been 0.94 kg/min for a number of reasons associated with the reliability of the fueling station. Frequent compressor and other hardware issues have caused the fill times to extend while operators wait to have a slow-fill deliver a sufficient quantity of hydrogen to provide adequate operating time for the buses. These buses use a significant quantity of hydrogen and when the station operates as designed, the fill times have been demonstrated to be acceptable to the commercial user.
- **Milestone 8: Demonstrate the ability to achieve 250-mile range without impacting passenger cargo compartment. (4Q, 2008)**
The Detroit Commuter Hydrogen Demonstration buses are not expected to perform to the same standards as a consumer designed fuel cell vehicle, but the demonstrated range in shuttle bus operation is more than adequate for project operation. Specifically, the two buses have provided 9.8 miles/kg of hydrogen, and in these buses, this produces a useable range of around 270 miles. This performance permits a single fill for each day of fleet use and is more than acceptable to the fleet operator. The H2ICE bus configuration in this project accommodates nine passengers compared to similar propane/gas-powered shuttle buses that can carry 10 passengers.
- **Milestone 14: Validate achievement of a refueling time of 3 minutes or less for 5 kg of hydrogen at 5,000 psi using advanced communication technology. (2Q, 2012)**
As noted in the discussion of fill times above, although communications technologies are employed, the reliability of the filling station has made it difficult to demonstrate achievement of this target. Assuming the best fill times of 1.4 kg/min as potentially viable in the process as designed, and using the communication technology that is employed at the station, the process would deliver 5 kg of hydrogen in 3.6 minutes.

Accomplishments

- Operated two H2ICE buses for 20,130 miles with high reliability.
- Demonstrated fuel economy of 9.6 to 9.8 miles/kg H₂.
- Carried over 6,560 passengers in regular airport shuttle service.
- Collected rider comment survey cards from 759 passengers with written comments from 325 passengers.
- Demonstrated overwhelming rider acceptance of the hydrogen power concept used in these H2ICE buses: 88.4% indicated this is an important environmental project and 99.6% indicated they would ride again on hydrogen-powered buses.
- Demonstrated that the H2ICE bus has comparable fuel economy, expressed in miles per gallon of gasoline equivalent energy, to the propane/gas-powered buses currently in use.

Introduction

SEMOG is exploring the development of a mass transit rail system to link Detroit with Ann Arbor and other southeast Michigan cities. If the public rail system is implemented, the Detroit Metropolitan Airport will be a key element of the system, and there will be a need to connect it to the commuter rail system at a station not too distant from the airport terminals. H2ICE vehicles could be used to link to the rail line at a proposed stop four miles from the airport.

This project is designed to evaluate the performance of H2ICE shuttle buses that can provide this passenger linking capability. Ford Motor Co. has developed a hydrogen powered V-10 engine and installed it into a shuttle bus chassis and body with a specially designed, multi-tank hydrogen storage system capable of holding 30 kg of hydrogen at 350 bar (5,000 psi).

Approach

Ford Motor Co. has applied hydrogen fuel technology to internal combustion engines and has built and delivered two buses powered by hydrogen fuel. These buses are designed to carry nine passengers with their luggage in normal airport shuttle service. Detroit Metro Airport has provided these buses to their ground transportation sub-contractor, Metro Cars Inc. Ford and BP, the fuel station operator, provided training in unique and safe operating procedures to METRO CARS® bus operators. METRO CARS® is operating and maintaining the buses in normal passenger service in airport parking operations.

Fueling is being done at a nearby City of Taylor hydrogen fueling facility. Bus operators are providing manual data collection, and Ford has installed on-board telemetry systems to collect real-time data about the buses operation and fuel use. Both the manual and telemetry data is being analyzed to determine the fuel economy of the hydrogen-powered buses, and to compare these two buses with similar propane/gasoline-powered buses operating in the same passenger carrying fleet. At the same time, survey cards are being provided to passengers to permit them to express their impression of the buses and their reaction to this hydrogen fuel initiative.

Results

The hydrogen-powered buses have been operating effectively since March 29th, 2009. They have accumulated over 20,000 miles in 126 operating shifts, and have carried over 6,500 passengers. This has permitted the collection of fuel use data and passenger comments to directly assess the viability of this technology in a regional transportation system.

Table 1 illustrates the fuel economy of the buses and compares the hydrogen-powered buses to two propane/gasoline-powered buses in the fleet. The data, both operator log and telemetry data, indicates that, on a gasoline gallon equivalent (gge) basis, the hydrogen buses are comparable to the propane buses.

TABLE 1. Comparative Fuel Economy Data
(Data from March 29 thru June 30, 2009)

Bus No.	820	830	32	41
Passenger Capacity	23	10	9	9
Fuel Type	Propane/Gasoline	Propane/Gasoline	Hydrogen	Hydrogen
Miles Driven	20,432	15,973	9,473	10,735
Hydrogen Used (kg)	0	0	978	1,111
Propane used (gal)	2,164	1,284	0	0
Propane GGE Used	1,581	938	0	0
Gas Used (gal)	899	597	0	0
Total GGE Used	2,480	1,535	986	1,120
MI/GGE	8.2	10.4	9.6	9.6
Telematics Fuel Used thru 7/05/09 kg			1,007.2	1,138.6
Telematics m/gge 7/05/09			9.7	9.9

The data can also be normalized for estimating the fuel economy under the assumption that all the buses in the study carried the same average number of passengers,

providing a somewhat more direct comparison. The largest (23-passenger) bus carries the highest average number of people (six) and is used as the standard for comparison. The reduction in the calculated fuel economy, for the hydrogen buses and for the 10-passenger propane/gas bus, is estimated by the percentage of weight change due to added passengers to estimate six passengers loading. Table 2 illustrates this calculation.

Passengers have reacted overwhelmingly positively to the hydrogen-powered bus concept. Their comments have been collected on survey cards provided to them by the bus drivers. 759 of 6,566 people who have ridden the buses through June 30th (11%) completed some or all of the survey questions. Tabel 3 is the summary of their input.

Conclusions and Future Directions

Conclusions

- The H2ICE concept is proving to be adaptable to shuttle bus operations.
- Fuel use and economy in shuttle buses is comparable to the current propane/gasoline-powered vehicles.
- No safety problems or concerns have arisen during this project, but continued operations will enhance

the understanding of potential safety issues should they occur.

- There have been no significant maintenance issues with the hydrogen buses and continued operation will provide more learning to support this comparison with conventional buses.
- Riders overwhelmingly accept both the buses and the application of hydrogen as a fuel for use in public transportation.

Future Directions

- Continue passenger service to enhance the data with operations in summer weather conditions.
- Explore alternative fueling options to overcome a potential early termination if the Taylor hydrogen facility does not remain open for the duration of this project.

FY 2009 Publications/Presentations

A poster presentation was made at the 2009 Annual Hydrogen Program Merit Review and Peer Evaluation Meeting in May. The SEMCOG team was represented and reported that there was attendee interest in the project and this application of hydrogen in the internal combustion engine-powered buses.

TABLE 2. Fuel Economy Estimate at Standard Passenger Load

Bus (passengers capacity)	Fuel	Reported Average Fuel Economy (FE)	Average number of passengers	% Weight increase/ FE Reduction at 6 passengers	Est. FE (mi/gge) at 6 Passenger Load
No. 820 (23)	Propane/Gas	8.2	6	0%	8.2
No. 830 (10)	Propane/Gas	10.4	3	7%	9.7
H ₂ Buses (9)	Hydrogen	9.8	2	6%	9.2

TABLE 3. Rider Survey Summary

Thru 7/5/09	Seats	Temperature	Clean	Smooth	Noise	Ride	Environmental Importance?		Ride Again?	
Very Good	567	470	574	459	587	560	Very Important	609	Yes	699
Good	147	177	97	275	148	173	No Opinion	74	No	3
OK	19	34	9	1	2	0	Not Important	22		
Not Good	4	5	0							
total	737	686	680	735	737	733		705		702

Thru 7/5/09	Seats	Temperature	Clean	Smooth	Noise	Ride	Environmental Importance?		Ride Again?	
Very Good	76.93%	68.51%	84.41%	62.45%	79.65%	76.40%	Very Important	86.38%	Yes	99.57%
Good	19.95%	25.80%	14.26%	37.41%	20.08%	23.60%	No Opinion	10.50%	No	0.43%
OK	2.58%	4.96%	1.32%	0.14%	0.27%	0.00%	Not Important	3.12%		
Not Good	0.54%	0.73%	0.00%	0.00%	0.00%	0.00%				

VIII.11 TDX Foundation Hydrogen Project*

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Contract Number: DE-FG36-08GO88096

Subcontractor:

Alaska Center for Energy and Power, Fairbanks, AK

Partners:

- National Renewable Energy Laboratory (NREL), Golden, CO
- Los Alamos National Laboratory, Los Alamos, NM

Project Start Date: September 15, 2008

Project End Date: March 30, 2010

*Congressionally directed project

(B) Hydrogen Storage

(C) Lack of Hydrogen Refueling Infrastructure
Performance and Availability Data

(H) Hydrogen from Renewable Resources

Contribution to Achievement of DOE Technology Validation Milestones

This project will contribute to achievement of the following DOE milestones from the Technology Validation section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- **Milestone 33:** Validate an electrolyzer that is powered by a wind turbine at a capital cost of \$655/kWe and 62% efficiency including compression to 5,000 psi with quantities of 1,000. (3Q, 2009)

Approach

St. Paul Island could produce fuel for transportation with its abundant wind energy resource. Hydrogen could be the fuel of the future. Our approach is to make site visits to active hydrogen fueling stations and public transportation projects to collect real data and stories. Lessons learned by visiting facilities, site managers, fueling attendants, bus drivers, and bus riders face-to-face cannot be found on Web sites. We will visit the wind-to-hydrogen electrolysis project at NREL for operational information.

A procurement study will provide a vendor and price list for a future demonstration project. Hydrogen production equipment, a fueling station, and a variety of hydrogen internal combustion engine (ICE) and fuel cell vehicles will be researched for comparison. Other alternative fuel vehicles, i.e., hybrid electric and plug-in electric vehicles, and fuel efficient gasoline and diesel trucks will be included for further comparison. An economic analysis will determine our demonstration project of choice. We recognize community education as a critical piece of this project and include two St. Paul Island workshops and school events to include hydrogen production and vehicle education, electric vehicle education, and to present our findings from this project.

Accomplishments

- Discovered that current system designs are cost prohibitive relative to the existing transportation system. For example, it costs \$1,355,000 for an

Objectives

- Quantify how much wind energy is available at existing wind-diesel plant compared to how much is needed to power transportation in addition to heat and lights.
- Optimize the use of wind energy to produce fuel for transportation.
- Demonstrate the technical and economic feasibility and commercial availability of appropriate technology for non fossil fuel forms of transportation on St. Paul Island.

Technical Barriers

This project addresses the following technical barriers from the Technology Validation section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) Lack of Fuel Cell Vehicle Performance and Durability Data

electrolyzer of the size we would need. This does not include the cost for the compressor, storage, and dispensing equipment.

- Discovered that there is limited availability, if any, of hydrogen ICE and fuel cell vehicles.
- Discovered that plug-in electric vehicle technology is available today, advancing rapidly, and looks to be economically feasible.

Future Directions

- Hold community outreach event in St. Paul to present findings. Include workshops on hydrogen, electric vehicles, and reasons for transition.
- Identify system design for charging station for plug-in electric vehicles.
- Identify and demonstrate plug-in electric vehicles.

FY 2009 Publications/Presentations

1. 2009 DOE Hydrogen Program Review, May 2009.

VIII.12 Texas Hydrogen Highway - Fuel Cell Hybrid Bus and Fueling Infrastructure Technology Showcase*

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Contract Number: DE-FG36-08GO88117

Subcontractors:

- University of Texas (UT) at Austin, Center for Electromechanics (UT-CEM), Austin, TX
- Gas Technology Institute (GTI), Sugar Land, TX, and Des Plaines, IL
- Center for Transportation and the Environment (CTE), Atlanta, GA
- Houston Advanced Research Center (HARC), The Woodlands, TX

Project Start Date: September 1, 2008

Project End Date: September 1, 2009

*Congressionally directed project

- (A) Lack of Fuel Cell Vehicle Performance and Durability Data
- (B) Hydrogen Storage
- (C) Lack of Hydrogen Refueling Infrastructure Performance and Availability Data
- (D) Maintenance and Training Facilities
- (E) Codes and Standards

Contribution to Achievement of DOE Technology Validation Milestones

This project will contribute to achievement of the following DOE milestones from the Technology Validation section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- **Milestone 11:** Decision to proceed with Phase 2 of the learning demonstration (2Q, 2010)
- **Milestone 14:** Validate achievement of a refueling time of 3 minutes or less for 5 kg of hydrogen at 5,000 psi using advanced communication technology. (2Q, 2012)
- **Milestone 24:** Validate a hydrogen cost of \$3.00/gge (based on volume production). (4Q, 2009)
- **Milestone 25:** Validate refueling site compression technology provided by the delivery team (4Q, 2012)
- **Milestone 26:** Validate refueling site stationary storage technology provided by the delivery team. (4Q, 2012)
- **Milestone 32:** Validate the ability to produce 5,000 psi hydrogen from natural gas for \$2.50/gge, untaxed and with large equipment production volumes (e.g. 500 units/year) for 1,000 hours. (3Q, 2011)

Objectives

- To provide public outreach and education by showcasing the operation of a 22-foot fuel cell hybrid shuttle bus and Texas's first hydrogen fueling infrastructure.
- To showcase operation of zero-emissions vehicle for potential transit applications.
- To advance commercialization of hydrogen-powered transit buses and supporting infrastructure.

Technical Barriers

This project addresses the following technical barriers from the Technology Validation section 3.6 of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

Approach

This project was originally developed to show that a skid-mounted, fully-integrated, factory-built and tested hydrogen fueling station could help simplify and lower the cost of fueling infrastructure for fuel cell vehicles. The project approach was to design, engineer, build, and test the integrated fueling station at the "factory", then install it at a site that offered educational and technical resources, and provided an opportunity to showcase both the fueling station and advanced hydrogen

FIGURE 1. Fuel Cell Plug-in Hybrid Shuttle Bus, Austin, Texas

vehicles. Through five years of project development, in coordination with various public and private sector sponsors, the site selected for a fuel cell bus and fueling station was Austin, Texas. Project participants are using these hydrogen technology assets in the current project for outreach and education to Texas target audiences on hydrogen and fuel cell application. This illustrates the potential for commercialization of hydrogen-powered transit buses, fueling infrastructure and related technologies. The project also showcases modeling techniques that can be used to design hydrogen vehicle and fueling solutions for other locations and applications.

The bus (Figure 1) and station (Figure 2) are housed at the Pickle Research Center, University of Texas at Austin located in north Austin. In addition to the fueling station, the project showcases a plug-in hybrid electric fuel cell transit bus that can operate in a real-world commercial application. It serves to validate the potential for transit agencies (and others) to operate similar vehicles thereby reducing emissions and the nation's dependency on foreign sources of energy for transportation fuels.

Accomplishments

- Preparation for commissioning fuel station in fall 2009:
 - The project team has expended considerable effort to prepare for start-up of the station in Austin.
 - Performance and safety checks have been conducted on the system during initial start-up and resulting in the following issues:
 - Pressure fluctuations in the system during automated start-up has led to on-site adjustment of the system controls.
 - Communications network link problems at the University of Texas led to a station

FIGURE 2. Hydrogen Fuel Station, Austin, Texas

computer system crash and subsequent need to reprogram the hydrogen station automated controls.

- The hydrogen station storage and dispensing system have been purged with hydrogen and test “fills” have been accomplished from the station to the fuel cell bus.
- Held station showcase events for limited, invited visitors which included bus rides and station tours.
- Planning for three to four Texas showcase events in fall 2009 and early 2010 in coordination with various target groups.
- Conducted briefing for Texas legislative staff on Texas Hydrogen Highway project.
- Collaborated on fuel cell bus and electrified transportation modeling:
 - UT-CEM collaborated with the UT Department of Mechanical Engineering on advanced energy storage and modeling techniques of electrified vehicles, including Powertrain System Analysis Toolkit (PSAT) model development of the Ebus and studies of ultracapacitor-assisted batteries.
 - UT-CEM assisted Georgia Tech on battery modeling method in PSAT for advanced, electrified transportation.
- Prepared two papers for publication (Institute of Electrical and Electronics Engineers [IEEE] and the Journal of Power Sources):
 - Paper accepted for the IEEE Vehicle Power and Propulsion Conference 2009 conference on PSAT modeling and evaluation of the Ebus.
 - A paper on the project was presented to the Texas Chapter of the American Society of Civil Engineers in Fall, 2008.
 - Paper under preparation in collaboration with Georgia Tech, for submission to the Journal of

Power Sources on advanced battery modeling for electric and hybrid electric vehicles.

Future Directions

- Finalize safety plan for submittal to DOE.
 - Continue preparation of fuel station for commissioning (late September 2009 to mid-October 2009).
 - Hold commissioning trials (3 months).
 - Conduct bus training for transit personnel.
 - Continue monitoring and evaluation of station and bus operations.
- Complete the final PSAT modeling of transit route to verify vehicle suitability for deployment.
 - Plan and conduct outreach and education events:
 - Station commissioning event.
 - Demonstration event in coordination with Austin, Texas event.
 - Review and selection of other outreach opportunities in Texas.
 - On-site demonstrations and education.

VIII.13 Florida Hydrogen Initiative*

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Contract Number: DE-FC36-04GO14225

Project Start Date: July 1, 2006
Project End Date: November 15, 2010

*Congressionally directed project

Background

The Florida Hydrogen Initiative, Inc. (FHI) is a nonprofit corporation that uses its resources to aid the development of a robust Florida-based hydrogen industry. The FHI seeks to develop Florida's hydrogen infrastructure by:

- Brokering partnerships for applied technology demonstration projects throughout Florida;
- Sponsoring research in the production, storage, and use of hydrogen fuels; and
- Facilitating technology transfers between the public and private sectors to create, build, and strengthen high-growth potential, high technology companies.

The FHI is a grantee of the U.S. Department of Energy Hydrogen Program and in the past year has funded and administered three projects:

1. The Hy-Tech Rest Area project is being conducted by EnerFuel, Inc., which will demonstrate the use of hydrogen derived from citrus waste in a fuel cell located at a Florida Turnpike rest area.
2. Designing and building a museum exhibit to tour 18 Florida science museums to inform and educate the public about hydrogen's potential and use as an energy carrying medium and the future role of

hydrogen in energy distribution. This project is being conducted by the Orlando Science Center.

3. The On-site Reformation of Diesel Fuel for Hydrogen Fueling Station Application project is being conducted by the University of Central Florida, Florida Solar Energy Center in partnership with Chevron Technology Ventures. The goal of this research is to develop a cost-effective energy efficient fuel reformation process that can be used for the production of high-purity hydrogen from sulfurous liquid fuels. Once developed, this process will be used in hydrogen fueling stations and remote fuel cell-based electrical generation stations in areas with no access to natural gas.

Each of the three projects' annual reports is provided in the following.

I. Hydrogen Technology (Hy-Tech) Rest Area

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Start Date: October 1, 2006
Projected End Date: March 31, 2010

Objectives

- Design, construct and demonstrate a 10 kW_{net} proton exchange membrane fuel cell stationary power plant operating on citrus-derived methanol.
- Achieve an electrical energy efficiency >32%.
- Demonstrate transient response time <3 ms.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of hydrogen, Fuel Cells, and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (C) Performance
- (E) System Thermal and Water Management
- (G) Startup and Shut-down and Energy/Transient Operation

Contribution to Achievement of DOE Technology Validation Milestones

This project will contribute to achievement of the following DOE technology validation milestones from the Technology Validation section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- **Milestone 35: Validate \$1.60/gge hydrogen cost from biomass and \$3.10/kg for renewable/electrolysis at the plant gate.** This project will assess the sources and economics of bio-derived methanol in Florida.

Accomplishments

- Completed direct methanol fuel cell (DMFC) vs. indirect methanol fuel cell (IMFC) trade study.
- Selected the Florida's Turnpike Enterprise's Turkey Lake Service Plaza as demonstration site.
- Obtained four, 5 kW_{net} IMFC power plants.
- Completed benchmark testing of fuel cell power plants.
- Obtained National Environmental Policy Act (NEPA) approval for construction phase.
- Completed layout and design of construction site including selection of dual-wall methanol storage tank and fire suppression system.
- Completed first draft of civil and electrical construction plans.
- Identified commercial producer of bio-methanol able to supply entire amount of fuel necessary to complete demonstration phase.
- Completed inverter software upgrade to allow co-generation operation of fuel cell power plant with the Turkey Lake Service Plaza facility.

Introduction

The use of biomass waste or the waste stream from bio-fuel production as a source of fuel for the generation of electrical power would be a significant benefit to the environment and provide additional feedstock for hydrogen fuel cells. The EnerFuel project aims to determine the effect of bio-diesel waste derived methanol on long-term fuel cell power plant performance and assess requirements for future projects and commercialization. By designing, constructing, and operating a 10 kW_{net} stationary fuel cell power plant in a co-generation mode, at the Florida Turnpike's Turkey Lake Service Plaza, the project will demonstrate the value of bio-methanol produced from a low value waste stream as a viable source of fuel for the generation of electrical power.

Approach

EnerFuel will identify sources of bio-methanol, arrange for transportation and storage, and establish safety protocols for the use and handling of methanol. They will obtain all of the required permits and prepare the demonstration site for power plant installation, including the electrical interface and methanol storage. They will design, construct, test and benchmark the fuel cell power plant and install and operate it at the Florida Turnpike Turkey Lake Service Plaza. The analysis of the fuel cell power plant under operation will determine the overall electrical efficiency, document system transient response to load changes, determine the effects of bio-diesel waste derived methanol on long-term power plant performance, and assess requirements for future commercialization.

Results

Due to recent economic shifts in the value of citrus waste and improvements in ethanol produced from citrus waste, the attractiveness of citrus derived methanol as an inexpensive fuel is no longer being considered. With increases in the price of cattle feed, citrus waste derived feed, once a low margin product, has become a product of higher value. In addition, ethanol producers that utilize citrus waste have improved their process resulting in the generation of significantly less methanol by-product. These factors diminished the viability of citrus-derived methanol as an inexpensive fuel. After a renewed search EnerFuel identified an alternate provider capable of producing commercial quantities of bio-methanol. BioMCN, a Netherlands company, is producing commercial quantities of bio-methanol from the glycerin by-product of bio-diesel production and selling it at competitive commercial methanol prices. EnerFuel will utilize this source of bio-methanol to demonstrate the feasibility of using low value renewable feedstocks to generate low cost electrical power.

The project selected the demonstration site and secured the support of the Florida Turnpike Enterprise for fuel cell co-generation of electrical power for the rest area facility. The inverters purchased to provide the necessary 208V, 3-phase power are being configured to provide the controllability and functionality necessary to allow the fuel cell systems to operate in a co-generation mode. An upgraded version of the manufacturer's firmware was installed in the inverters and its ability to allow co-generation operation verified on an in-house test rig (Figure 1). The entire power plant including IdaTech fuel cells (Figure1), inverters and batteries will be tested in-house prior to installation at the Turnpike rest area.

The locations of the power plant and the methanol storage container have been selected and the survey of

the electrical interface requirements has been completed. NEPA approval was obtained and permitting work started. A final review of the site layout and construction plans is underway to assure all mechanical and electrical requirements for the demonstration have been covered. The plans will then be submitted to the permitting office in Orange County, Florida as well as submitted to the Florida State Fire Marshal's office for approval.

The cost for purchasing and transporting the bio-methanol from BioMCN has been identified. Once site construction is underway the entire amount of methanol will be ordered and delivered directly to the demonstration site.

IdaTech 5kW_{net} indirect methanol fuel cell

Inverter test rig

FIGURE 1. IdaTech 5 kW_{net} IMFC System and Inverter Test Rig

Conclusions and Future Directions

- The project has selected the technical approach for using bio-diesel waste derived methanol for the fuel cell power plant and identified the cost and logistics for transporting the fuel to the demonstration site.
- EnerFuel is currently configuring the inverters, batteries and fuel cell system to properly function in a co-generation mode prior to installation at the Turnpike Turkey Lake Service Plaza site.
- A final review of the site layout and construction plans is underway prior to submission for county permitting and fire marshal approval.
- Construction of the demonstration site is estimated to commence in November of 2009 with operation of the fuel cell power plant expected to begin in mid-December 2009.

II. Assessment of Public Understanding of the Hydrogen Economy Through Science

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Project Start Date: July 31, 2006

Project End Date: September 30, 2008

Objectives

- Design and build an interactive exhibit "H2Now: the Great Hydrogen Xchange."
- Assess current public understanding about hydrogen science and engineering.
- Increase public understanding of hydrogen science and engineering.

Technical Barriers

This project addresses the following technical barriers from the Education section (3.9.5) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) Lack of Readily Available, Objective, and Technically Accurate Information
- (B) Mixed Messages
- (C) Disconnect between Hydrogen Information and Dissemination Networks
- (E) Regional Differences

Contribution to Achievement of DOE Education Milestones

This project will contribute to achievement of the following DOE milestones from the Education section (3.9.7) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- **Milestone 11 – Develop set of introductory materials suitable for a non-technical audience.** (4Q, 2006) The interactive exhibit, titled “H2Now: the Great Hydrogen Xchange incorporates basic information about hydrogen and its use as an alternative energy source. Learning outcomes include:
 - Defining what hydrogen is, where it comes from, and many of its possible uses.
 - Determining fact from fiction that surrounds hydrogen as a renewable energy source.
 - Listing some benefits of using hydrogen as an alternative energy source.
 - Describing how hydrogen energy is created and how it can affect daily life.

Accomplishments

- Opening of H2Now: the Great Hydrogen Exchange at the Orlando Science Center on August 15, 2009.
- Extensive testing of mechanical and software effectiveness with periods of mechanical and software remediation between August, 2008 and February, 2009.
- Visitor testing to determine educational effectiveness against educational objectives completed April, 2009.

Introduction

Finding sources of clean, renewable energy is one of today's most pressing issues. However, there is much information – and misinformation – about renewable energy, particularly regarding the use of hydrogen as a new energy source. Increasing the basic knowledge and awareness among the public about hydrogen as a viable energy source, and correcting misconceptions of hydrogen and its properties, is necessary to create accurate and positive opinions about this substance as an important alternative to fossil fuels.

Key to this goal is the accurate and educationally effective translation of technical scientific and engineering concepts into a format that is easily understandable and accessible. In H2Now: the Great Hydrogen Xchange, visitors will be able to imagine a

community powered entirely by hydrogen, and discover that the renewable energy source is a viable alternative to other energy sources currently in use.

Approach

Working with I.d.e.a.s at Disney MGM Studios, the Orlando Science Center (OSC) set out to perform front end evaluation and subsequent design, fabrication, and installation of an interactive exhibition at the OSC. Beginning with the schematic design of concepts and educational objectives, the exhibit will undergo design and prototyping of both physical components and interactive software. This exhibition, H2Now, the Great Hydrogen Xchange, contains two main interactive areas. The first, the H2 Charging Stations, visitors will have the opportunity to express their opinions about alternative energy sources, and interact with increasing levels of content about hydrogen as a new source of fuel. As they answer questions correctly about hydrogen, they earn Hydrogen Energy Units (HEUs) that they can ‘spend’ at Hydropolis to power various interactive ‘city’ elements.

Results

From mid-August through December 2008, software developers at I.d.e.a.s, working with OSC staff, incorporated several changes to the software design and interface based on critical analysis of visitor usage to test for mechanical effectiveness. At the end of that time, it was determined that major modifications were needed to both software design and communication interface. OSC brought in a local multimedia design firm to complete this redesign at which time visitor evaluation to determine extent to which the affective and cognitive goals of the exhibit were met.

With the exhibition now installed and fully operational at OSC, additional exhibit enhancements have been made including a linear display on additional sources of renewable energy and plans are in the works for an interactive ‘video game’ on renewable energy to complement the messages of H2Now.

Conclusions and Future Directions

- The H2Now exhibit has completed software and hardware ‘shakedown’ that resulted in a streamlined interface and communication and is functioning at 100% in the OSC.
- Summative evaluation to determine the extent to which H2Now meets educational objectives revealed that:
 - 77% of the visitors surveyed either loved the exhibit or liked the exhibit.

- Nearly 64%, in the word choice section of the interview, indicated that they ‘learned something’ or found the exhibit ‘informative’.
- Nearly 32% found the exhibit ‘interesting’ indicates that both cognitive and affective learning has clearly taken place.
- Additionally, 65% indicated that they found out something they didn’t know before. This finding is a clear indication of both cognitive gain and a change of attitude i.e., compare this to the 44% who, when given the choice to select “I learned something new”.
- OSC has enhanced the experience with the short film produced by i.d.e.a.s called “I Am Hydrogen” and is exhibiting a linear display on additional information on renewable energy. OSC has received a grant from Progress Energy to produce an exhibit enhancement piece – a video game on renewable energy.

III. On-Site Reformation of Diesel Fuel for Hydrogen Fueling Station Applications

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Project Start Date: January 21, 2008
 Project End Date: June 20, 2009

Objectives

- Develop efficient and stable catalysts for hydro-reforming of high-sulfur diesel and other liquid hydrocarbon fuels to sulfur-free light hydrocarbons (C_1 - C_4) that can be readily reformed with steam to hydrogen.
- Develop, test and validate a viable desulfurization process suitable for on-site scrubbing of high sulfur gas for forecourt applications.
- Demonstrate continuous operation of an integrated process for pre-reformation of high sulfur diesel

coupled with a hydrogen sulfide scrubber for generating a mixed gas containing light molecular weight hydrocarbons and less than 10 ppmv H_2S impurity.

Technical Barriers

This project addresses the following technical barriers from the Technology Validation section (3.6.4) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration:

- (C) Lack of Hydrogen Refueling Infrastructure Performance and Availability Data

Contribution to Achievement of DOE Technology Validation Milestones

This project will contribute to achievement of the following DOE Technology Validation milestones from the Technology Validation section of the HFC&IT Program Multi-Year Research, Development and Demonstration Plan:

- **Milestone 24:** Validate a hydrogen cost of \$3.00/gge (based on volume production). (4Q, 2009).

Accomplishments

- A novel process has been developed for converting high-sulfur diesel to a mixture of light molecular weight hydrocarbons that can be readily reformed with steam to fuel cell grade hydrogen gas. The catalytic pre-reformer was coupled with a re-generable Fe^{2+}/Fe^{3+} redox/electrolysis unit capable of scrubbing H_2S from the pre-reformer effluent in the form of hydrogen gas and elemental sulfur.
- An electrolytic process for oxidation of the acidic $FeSO_4$ aqueous solution has been developed having a columbic efficiency of 100% at a cell voltage of 1.0 V, and without using platinum as anode material.
- A robust bi-functional catalyst was developed for pre-reforming of high-sulfur fuels (sulfur content as high as 5,240 ppmw) to short chain hydrocarbons (C_1 - C_4 , mostly, propane) at an average yield of 97%.
- The combined Fe^{2+}/Fe^{3+} redox/electrolyzer and high-sulfur fuel pre-reformer was operated successfully for 100 hours, continuously, achieving desulfurization efficiencies greater than 95% and removing sulfur down to less than 5 ppmv in the pre-reformate.

Introduction

One major challenge facing the future hydrogen economy is how to deliver H_2 fuel within the transportation sector. If hydrogen is to be derived from high energy feedstocks, it may be desirable to transport the feedstock itself to local fueling stations and convert the material on-site. Furthermore, it would be advantageous if the primary feedstock can be used as a fuel in the legacy vehicular power plants (e.g., internal combustion engines [ICEs], etc.). For example, diesel fuel could be delivered via tanker truck and converted in a small reformer on-site for generating and dispensing H_2 at the fueling station. There are many advantages to this approach including:

- Existing delivery infrastructure (highway to fueling station) could be utilized.
- More energy can be delivered per trip when the tanker is filled with diesel instead of liquid hydrogen.
- The fueling station would be able to service both ICE- and fuel cell-powered vehicles simultaneously.
- The fueling station operation would be flexible and easily change fuel availability in the form of hydrogen or diesel fuel to meet the customer demand.

Reforming high-sulfur hydrocarbon fuels (e.g., diesel fuel, JP-8, sub-quality natural gas, etc.) is particularly challenging due to rapid deactivation of conventional reforming catalysts by coke deposits and sulfurous compounds. Moreover, if sulfurous compounds (mostly, H_2S) are not removed from pre-reformate they deactivate the steam reforming catalyst used for hydrogen production. In a joint effort involving the Florida Solar Energy Center (FSEC) and Chevron Technology Ventures (CTV), a new on-demand hydrogen production process for the fueling station applications has been developed and validated. The objective of this work was to convert high-sulfur hydrocarbon fuels to an essentially sulfur-free gas suitable for steam reformation, while consuming only a small fraction of the hydrogen produced. The removal of sulfur from reformate is critical since most catalysts used for the steam reformation have limited sulfur tolerance. FSEC was tasked to build, operate and validate the performance of the pre-reformer as well as to develop and demonstrate a viable desulfurization unit capable of S-scrubbing of the pre-reformer effluent on-site at the filling stations. CTV provided a catalyst for the pre-reforming stage and assisted with the design of the pre-reformer.

Approach

The approach to meet the project objectives targeted at integrating a high-sulfur fuel pre-reformer with a desulfurization system. First, the high-S fuel is pre-reformed, catalytically, to short chain hydrocarbons (i.e.,

C_1 - C_4) by hydrodesulfurization. In the pre-reformer, most sulfurous species present in the fuel convert to hydrogen sulfide (H_2S). This step is necessary in order to avoid deactivation of the Ni-based catalyst used in the steam reformer further downstream. Removing hydrogen sulfide from the pre-reformer effluent occurs in a special regenerative redox system that uses an iron-based scrubber paired with an electrolyzer. The sulfur-free gas emerging from the regenerative scrubber is fed to the main reformer, where it is mixed with steam and processed over a Ni-catalyst to syngas. This process precedes further treatment of the gas in a shift reactor followed by the pressure swing adsorption to separate H_2 for on-site storage and/or fueling vehicles. A rather small portion (10-15%) of the hydrogen produced in the process is returned to the pre-reformer and used to carry out hydrodesulfurization process in the pre-reformer.

Results

Pre-Reforming of High-Sulfur Hexadecane and Diesel Fuel

Figure 1 shows a simple block-diagram depicting the process used for the conversion of high-sulfur fuel to hydrogen gas.

A high-S hydrocarbon fuel (e.g., diesel) is heated and vaporized in a pre-heater (1) before entering a catalytic pre-reformer (2) wherein the fuel is hydro-reformed to shorter chain hydrocarbons (i.e., C_1 - C_4). In the pre-reformer all sulfur organics are converted to H_2S gas. Hydrogen sulfide removal from the pre-reformate is accomplished in a special regenerative system having a sulfur scrubber (4) coupled with an electrolytic regenerator (5). The sulfur-free gas from the desulfurization unit (4+5) is fed to the steam reformer (6), where it is processed over a Ni-catalyst to syngas that is mostly H_2 , CO and CO_2 . The syngas is further treated in a shift reactor and purified (via pressure swing adsorption process) (7) to high-purity hydrogen gas. Figure 2 depicts the bench-scale experimental unit built and used at FSEC to conduct the desulfurization of high-sulfur diesel fuel.

The pre-reformer consisted of: 1) fuel metering and delivery section, 2) pre-reforming reactor, 3) products separation unit, and 4) products metering and analysis section. In the fuel delivery section, a high performance liquid chromatography pump was used to pump the liquid fuel (diesel or hexadecane) into the reactor at flow rates in the range of 0.2-0.4 mL/min. Hydrogen gas entered the pre-reformer via a high-pressure mass flow controller set at flow rates in the range of 0.72-3.50 L/min. The 316 stainless steel pre-reforming reactor used in this work was a tube reactor having an inside diameter of 25 mm, wall thickness of 2 mm, and a length of 45 cm. Three quarters of the reactor was filled with catalyst. Hydrogen entered at the bottom of

FIGURE 1. A simple block-diagram depicting the process used for the conversion of high-S fuels to hydrogen gas.

FIGURE 2. Bench-scale diesel pre-reforming reactor coupled with a desulfurization unit.

the reactor and the reformate counter flowed from the top. The temperature in the upper section of the reactor was maintained at 400-450°C and in the lower part (where the fuel entered the reaction zone) at 450-500°C. In the products separation section, the effluent passed through a shell-and-tube type condenser (maintained at 15-20°C) where most of C₆+ hydrocarbons condensed and refluxed back into the reactor and the gaseous hydrocarbons (mostly, C₁-C₄), H₂S and excess H₂ allowed to exit and flow into a knock-out chamber where the fugitive heavier hydrocarbons were trapped and collected. The product gas then flowed through in-line filters, passing through a back-pressure regulator and into a gas metering and analysis section.

Several experiments were conducted employing zeolite catalyst, Ni-Mo/alumina catalyst and a mixture of zeolite and Ni-Mo/alumina catalyst. In these experiments, separate hydro-reformation of hexadecane and diesel over zeolite and Ni-Mo catalysts showed a gradual deactivation of the catalysts due to coke formation. However, a mixture of zeolite and Ni-Mo/

FIGURE 3. Product slate from the diesel hydro-reforming over zeolite/Ni-Mo catalyst at 450°C (left) and 500°C (right). (P = 13.7 atm)

alumina catalysts in the weight ratio of 2:1 performed very well. After about 16 hrs (through a 100-hr run), a steady-state condition was reached where the catalyst remained stable for the duration of the experimental run.

Figure 3 depicts the distribution of the high-sulfur diesel under two steady-state temperature regimes: 450°C and 500°C. Average conversions obtained in these experiments were in the range of 95-97%. The product distribution for the diesel and hexadecane hydro-reformation over the same catalyst and at the same temperature regime were similar. However, the diesel-derived gas contained slightly higher concentration of heavier hydrocarbons (C₆ - C₈+) compared to that derived from hexadecane. Figure 3 also shows that an increase in the pre-reformer temperature results in increased concentration of methane in the product.

Desulfurization of the Pre-Reformer Effluent

The analysis of the gas produced in the pre-reformer by the hydrogenation of the thiophene-laden hexadecane and diesel on zeolite/Ni-Mo catalyst indicated that

thiophene was almost quantitatively converted to H_2S . The pre-reformer effluent containing H_2 , H_2S and light hydrocarbons (mostly $\text{C}_1\text{-C}_4$) flowed to the regenerative desulfurization unit. Figure 4 depicts a schematic diagram of the desulfurization sub-unit used for continuous removal of hydrogen sulfide in the pre-reformer effluent and its conversion to H_2 and sulfur. A gaseous mixture from the pre-reformer enters into the scrubbing unit having an absorption column filled with aqueous ferric sulfate solution, $\text{Fe}_2(\text{SO}_4)_3$. When H_2S dissolves in the aqueous solution, it oxidizes by ferric ion (Fe^{3+}) to elemental sulfur, and at the same time ferric sulfate is reduced into ferrous sulfate, FeSO_4 . The elemental sulfur is removed from the flowing solution by a filter while the ferrous sulfate solution is fed to an electrolyzer. In the electrolyzer, ferrous sulfate is oxidized back to ferric state while, at the same time at the cathode, protons are reduced to hydrogen gas. The regenerated ferric sulfate solution is returned to the absorption column to scrub hydrogen sulfide – and thus, forming a closed cycle with the net reaction being hydrogen sulfide decomposition to elemental sulfur and hydrogen gas.

Electrolysis of acidic FeSO_4 aqueous solutions was carried out using a modified proton exchange membrane electrolyzer. The cathode section consisted of a stainless steel plate used as current collector in a contact with water for hydrogen evolution. This configuration eliminated the need for a carrier gas to sweep hydrogen from the cathode side of the electrolyzer. An electrolyzer potential of 0.80 to 1.03 volts was necessary for the electrochemical process to regenerate the scrubber solution at a rate sufficient to match the H_2S flow rate into the scrubber. The electrolytic system can be operated at the range of temperatures from ambient to 90°C . In our experiments, desulfurization of the pre-reformate gas occurred optimally at the following process

conditions: iron sulfate (total) concentration of 0.1 M, pH of 1.7-1.8 (adjusted by addition of 5 N sulfuric acid), and electrolyte temperature of 50°C .

The hydrogen evolution rate in the regenerative electrolyzer is a linear function of H_2SO_4 concentration (within the range of $[\text{H}_2\text{SO}_4] = 0.25\text{-}0.75\text{ N}$), but not so with respect to the FeSO_4 concentration – for which it goes through a maximum corresponding to $[\text{FeSO}_4] \sim 0.15\text{ M}$. This can be attributed to the generation of polysulfate species at higher concentrations that are less active in transferring charge at the anode.

During initial testing of the scrubber-electrolyzer system, the desulfurization unit operated continuously for more than 300 hours using a surrogate gas mixture that contained 2,500 ppmv H_2S (reminder nitrogen) as an input. The system performed well and practically no H_2S could be detected at the scrubber outlet (which corresponded to several turnovers of the $\text{Fe}^{2+}/\text{Fe}^{3+}$ -redox system). In the diesel pre-reforming experiment using the zeolite/Ni-Mo catalyst, diesel spiked with 3,180 ppmw of thiophene produced a product stream containing 185 ppmv of H_2S . The gas chromatograph analysis showed the presence of H_2S as the only product of hydrogenation of thiophene; no unreacted thiophene or other sulfurous compounds were present. On average, about 3 ppmv of H_2S was detected exiting the ferric sulfate scrubber during the run. A similar experiment using the zeolite-Ni-Mo mixed catalyst and hexadecane spiked with 5,240 ppmw thiophene produced largely desulfurized gas with the H_2S content of less than 5 ppmv.

The sulfur balance for the pre-reforming reaction and the degree of desulfurization was determined by comparing the molar mass of sulfur in the fuel entering the pre-reformer with the molar mass of H_2S detected in the scrubber exit gas. The sulfur balance for all tests conducted was closed within the margin of error of 6-8% using two independent methods for analyzing the H_2S gas (GC and gas-detection tubes). The fuel desulfurization yield was defined as:

$$\eta = \frac{(C_4H_8S)_{in} - (H_2S)_{out}}{(C_4H_8S)_{in}} \cdot 100\%$$

Where, η is fuel desulfurization yield, $(C_4H_8S)_{in}$ is number of thiophene moles in the fuel entering the pre-reformer, $(H_2S)_{out}$ is the number of H_2S moles leaving the sulfur scrubber.

Experimental data obtained from high-S diesel and hexadecane pre-reforming-desulfurization tests showed average desulfurization yields in the range of 96-98%.

Characterization of the Pre-Reforming Catalyst

Scanning electron microscope, X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD)

FIGURE 4. Schematic of a desulfurization unit including a scrubber and an electrolyzer.

analyses were employed to characterize zeolite/Ni-Mo catalyst before and after pre-reforming of high-sulfur diesel. The XPS spectrum of the $\text{Mo3d}_{5/2}$ and $\text{Mo3d}_{3/2}$ transitions for the oxidized form of Ni-Mo catalyst showed only Mo^{6+} species, corresponding to binding energies of 233 and 236 eV, respectively. After exposure of the catalyst to reducing and sulfiding environments, the reduced Mo^{4+} species appeared in the XPS spectrum with $\text{Mo3d}_{5/2}$ binding energy of about 229 eV. The peaks at 229-229.6 eV in the sulfided catalyst indicate the presence of MoS_2 . The spectrum showed that after hydro-reforming, a significant amount of Mo in the catalyst remained in its oxidized form implying that a strong interaction of oxidized Mo species with the alumina support did occur.

Interpretation of the Ni2p region of the XPS spectra as it relates to oxidized and reduced forms of the Ni-Mo/alumina catalyst was challenging, because of proximity of Ni2p binding energies for different Ni species. Indeed, it is difficult to distinguish between different Ni species (e.g., NiO, Ni_2O_3 , NiAl_2O_4) in the XPS spectrum, as all may appear in the same region. The weak peak at the binding energy of 854 eV in the reduced/sulfided form of the catalyst may be attributed to NiS. The absence of a peak at a binding energy of 852.4 eV indicated that nickel was not reduced to its metallic state, and most likely, remained in its Ni^{2+} oxidation state.

The XRD pattern of the Ni-Mo/alumina catalyst after high-sulfur diesel pre-reforming showed two prominent diffraction peaks appearing at 2θ values of 46 and 67 degrees that were assigned to $\gamma\text{-Al}_2\text{O}_3$. The XRD pattern did not show XRD-observable Ni oxides; however, it is commonly observed that NiO and Ni_2O_3 may exist in amorphous or microcrystalline phases. Identification of the NiAl_2O_4 phase is rather difficult because of the proximity of its reflection to that of alumina. Peaks corresponding to Mo compounds were apparently too weak to be distinguishable on the XRD pattern of the catalyst used.

Conclusions and Future Directions

- A novel process has been developed for converting high-sulfur diesel to a mixture of light molecular weight hydrocarbons that can be readily reformed with steam to fuel cell grade hydrogen gas. The process employs a catalytic pre-reformer coupled

with a regenerable $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox/electrolyzer system for the scrubbing of H_2S from the pre-reformer effluent and its conversion to hydrogen gas and elemental sulfur. Electrolysis of acidic FeSO_4 aqueous solution was highly efficient with a coulombic efficiency of 100% at a cell voltage of 1.0 V. It was shown that the electrolytic process can be operated with a Pt-free anode to oxidize ferrous to ferric ions, thereby reducing the cost of the electrolytic system, considerably.

- A robust bi-functional catalyst was developed for accomplishing the pre-reformation of the high-sulfur fuels (sulfur content as high as 5,240 ppmw) to short chain hydrocarbons ($\text{C}_1\text{-C}_4$, mostly propane) at an average yield of about 97%.
- The integrated $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox/electrolyzer H_2S scrubber and pre-reformer was operated successfully for 100 hours, continuously, achieving desulfurization efficiencies greater than 95% and removing sulfur down to less than 5 ppmv in the pre-reformer effluent.

Special Recognitions & Awards/Patents Issued or Pending

- Cunping Huang, Franklyn Smith, Clovis Linkous, Karthikian Ramasami, Ali T-Raissi, Nazim Muradov, "Method and System for Hydrogen Sulfide Removal," U.S. Patent Application No. 61/023,755.

FY 2009 Publications/Presentations

- Nazim Muradov, Karthikeyan Ramasamy, Cunping Huang, Ibrahim Adebisi, Franklyn Smith, Clovis Linkous, Ali T-Raissi and James Stevens, "Combined Pre-Reforming-Desulfurization of High-Sulfur Diesel for Hydrogen Fueling Station Applications", submitted to *J. Fuel*.
- Nazim Muradov, Karthikeyan Ramasamy, Cunping Huang, Ibrahim Adebisi, Franklyn Smith, Clovis Linkous, Ali T-Raissi, James Stevens, "Combined Pre-Reforming-Desulfurization of High-Sulfur Diesel for Hydrogen Fueling Station Applications", Presented at the 2009 AIChE Spring Meeting, Tampa, Florida (2009).
- Nazim Muradov, Karthikeyan Ramasamy, Cunping Huang, Ali T-Raissi, James Stevens, "Catalytic Processing of High-Sulfur Fuels for Distributed Hydrogen Production", submitted to *18 World Hydrogen Energy Conference*, Essen, Germany, 2010.

IX. SAFETY, CODES & STANDARDS

IX.0 Safety, Codes & Standards Sub-Program Overview

Introduction

Codes and standards development requires coordination of activities across government agencies, industry associations, corporate and international stakeholders, and codes and standards development organizations. To this end, the Safety, Codes & Standards Sub-Program leads collaborative domestic and international efforts to prepare, review, and promulgate the codes and standards needed to expedite hydrogen infrastructure development and to help enable the emergence of hydrogen as a significant energy carrier on a global scale.

The Safety, Codes & Standards Sub-Program supports research to provide a scientific basis for requirements incorporated in hydrogen codes and standards and facilitates the development of codes and standards for hydrogen use in transportation, stationary, and portable applications. This collaborative activity among government, industry, universities, and national laboratories is an integral part of an internationally supported effort. The activity also supports the development and implementation of practices and procedures to ensure safety in the operation, handling, and use of hydrogen and hydrogen systems for all DOE-funded projects.

The safety activity involves a large degree of external stakeholder input. Expertise is gathered from the energy, insurance; and aerospace industries as well as automobile manufacturers, the fire protection community, academia, and others to provide the widest possible range of safety expertise. Input is obtained through involvement in a variety of activities, as detailed under the Technology Status section.

Communication among codes and standards stakeholders is emphasized to maximize the impact of safety activities. All of the non-confidential data and information obtained through safety activities are made available through public presentations and the Program's online information resources. Safety information materials created to enhance the knowledge of emergency responders and local authorities are made available through various media to the largest number of safety personnel possible. In addition, planning efforts supporting future activities are conducted through open workshops to ensure stakeholders are properly and thoroughly engaged.

Goals

- Enable and facilitate the appropriate research, design, and development for the development of safe, performance-based, technical codes and standards that support technology readiness and are appropriate for widespread consumer use of fuel cell and hydrogen-based technologies.
- Facilitate the development and harmonization of domestic and international codes and standards. Complete research and development (R&D) to support essential codes and standards by 2010.
- Develop and implement the agreed upon safety practices and procedures that will ensure the safe operation, handling and use of hydrogen and hydrogen systems for all DOE projects and utilize these practices and lessons learned to promote the safe use of hydrogen.

Objectives

- Support and facilitate the completion of necessary codes and standards needed for the early commercialization and market entry of hydrogen and fuel cell energy technologies.
- Complete preliminary research and development on hydrogen release scenarios to support the establishment of setback distances in building codes, and provide a sound basis for model code development and adoption.
- Support and facilitate the effort, led by the National Fire Protection Association (NFPA), to complete the draft Hydrogen Technologies Code (NFPA 2) by 2010.
- Facilitate the adoption of the most recent, available model codes (e.g., International Code Council [ICC] and NFPA) in key regions through education and training for code officials.

- Develop a comprehensive safety plan in collaboration with industry that establishes Program safety policies and guidelines by 2010. DOE will utilize the Hydrogen Safety Panel's expertise and assistance in conducting safety evaluations and identifying safety-related technical data gaps, lessons learned and best practices.
- Promote the widespread sharing of safety-related information and knowledge tools with first responders (authorities having jurisdiction) and other stakeholders.
- Support and facilitate the development of Global Technical Regulations (GTR) for hydrogen vehicle systems under the United Nations Economic Commission for Europe, World Forum for Harmonization of Vehicle Regulations and Working Party on Pollution and Energy Program (ECE-WP29/GRPE) by 2010.

FY 2009 Technology Status

The Safety, Codes & Standards Sub-Program utilizes the expertise of the Hydrogen Safety Panel to evaluate the safety plans and practices of DOE-funded projects. This activity provides recommendations on the safe conduct of project work and lessons learned/best practices that can be of broad benefit to the DOE Hydrogen Program. The panel, its services and work products are assets to DOE-funded project teams who perform their own risk assessment and mitigation planning and are responsible for their own safe operating practices. In this manner, the panel helps to disseminate hydrogen safety best practices.

To help fill the void of publicly available hydrogen safety data, the Sub-Program has developed and published five online hydrogen safety information resources:

- The Hydrogen Incidents and Lessons Learned Database¹, developed by Pacific Northwest National Laboratory (PNNL), catalogs hydrogen incidents, near-misses and lessons learned from a variety of sources including DOE-funded projects.
- The Hydrogen Safety Bibliographic Database, developed by the National Renewable Energy Laboratory (NREL), was established in response to a recommendation from the National Research Council.² The Hydrogen Safety Bibliographic Database³ contains more than 500 publicly available hydrogen safety-related reports, papers, and presentations, allowing researchers, code officials, and stakeholders to learn from others' experiences.
- The Hydrogen Safety Best Practices Manual⁴ developed by PNNL and Los Alamos National Laboratory, contains nine hierarchical, peer-reviewed sections on best practices and is cross-referenced with the Hydrogen Incidents and Lessons Learned and Hydrogen Safety Bibliographic Databases.
- The Permitting Compendium for Hydrogen Facilities⁵, developed by NREL, is a one-stop information resource to facilitate the permitting of hydrogen fueling stations and stationary fuel cell installations.
- Technical Reference for Hydrogen Compatibility of Materials⁶, developed by Sandia National Laboratories, contains a compilation of hydrogen-compatible materials and properties.

In addition, the Safety, Codes & Standards and Education Sub-Programs launched an online *Introduction to Hydrogen Safety for First Responders* course. The seven-module, Web-based course provides an overview of hydrogen technologies and applications for fire, law enforcement, and emergency medical personnel. The Web-based course has averaged 300-500 unique visits/month and over 9,300 visits since its launch in January 2007.

¹ This resource is available at <http://www.h2incidents.org>.

² National Research Council, Review of the *Research Program of the FreedomCAR and Fuel Partnership*, Washington, D.C.: The National Academies Press, 2005, p. 39.

³ http://www.hydrogen.energy.gov/biblio_database.html/

⁴ <http://www.h2bestpractices.org/>

⁵ <http://www.hydrogen.energy.gov/permitting/>

⁶ <http://www.ca.sandia.gov/matlsTechRef/>

The Safety, Codes & Standards Sub-Program provides support for the International Partnership for a Hydrogen Economy and the International Energy Agency, both of which have been engaged in hydrogen safety work. Additionally, DOE continues to work with the Department of Transportation to support its role as U.S. representative to the UN GTR process.

FY 2009 Accomplishments

- Developed the technical basis for assessing the safety of hydrogen-based systems for use in the development and modification of relevant codes and standards, which has introduced a risk-informed approach for separation distances into NFPA 55 (Standard for the Storage, Use, and Handling of Compressed and Liquefied Gases in Portable Cylinders) 2009 code cycle in June 2009.
- Engaged members of the building code and fire safety community in the development of safety information tools for the permitting of hydrogen fueling stations and hydrogen fuel cells for telecommunications backup power. More than 250 code officials have been trained to date.
- Established better coordination among international teams and accelerated R&D to support the development of a draft international hydrogen fuel quality standard for proton exchange membrane fuel cells in road vehicles by 2010.
- The Hydrogen Safety Panel has reviewed more than 200 safety plans, and conducted 37 site visits and telephone interviews since its inception. The panel provides expertise and guidance to DOE and assists with identifying safety-related technical data gaps through technical white papers.
- Completed upgrade of Web-based *Introduction to Hydrogen Safety for First Responders*. This multimedia tutorial acquaints first responders with hydrogen, its basic properties, and how it compares with like fuels.
- Completed development and conducted inaugural advanced-level training course that includes a hands-on fuel cell vehicle prop. This course is the first of its kind in the United States and is aimed at first-responders dealing with hydrogen-related incidents, with more than 90 first responders from 18 states participating or on a waiting list.
- Updated and improved the online hydrogen safety databases including the Hydrogen Incidents and Lessons Learned Database, Hydrogen Safety Bibliographic Database, and the Hydrogen Safety Best Practices Manual.
- Published “H2 Safety Snapshot” as a topical newsletter.

Budget

The Sub-Program received an appropriation of \$12.5 M for Fiscal Year 2009. This funding allowed for sustained progress on hydrogen release behavior, hydrogen fuel quality, quantitative risk assessment, and leak detection research to support the codes and standards development process. In addition, work has started on a codes and standards gap analysis for the Vehicle Technologies Program.

The President’s FY 2010 budget realigns the Program to focus on nearer term priorities for our Nation’s most pressing energy needs. As part of the realignment, no funding for Safety, Codes and Standards was requested.

2010 Plans

The applied R&D program in the Office of Energy Efficiency and Renewable Energy will coordinate with the Office of Science, which plans to include up to \$50 M of basic research related to hydrogen and fuel cell technologies. In addition, through the projects funded by the American Recovery and Reinvestment Act of 2009 lessons learned, best practices related to hydrogen and fuel cell safety, codes and standards will be documented.

Final reports documenting progress will be issued in FY 2010. The Safety, Codes and Standards Sub-Program will continue to coordinate the efforts of codes and standards organizations to identify and address the gaps, clarify and consolidate regulations, validate outdated test results, and ultimately develop new, more appropriate codes and standards. The Sub-Program will be working with the

Department of Transportation and other hydrogen experts on a hydrogen and natural gas lessons learned workshop. The focus of this workshop will be to coordinate and harmonize lessons learned and activities among the compressed natural gas and hydrogen industry, stakeholders and experts. This workshop will provide a foundation to help shape the path forward in policy, regulation, and codes and standards. In addition the Safety, Codes & Standards Sub-Program will continue to perform research and development to minimize the knowledge gap in safety, and enable solid codes and standards to be developed.

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IX.1 Hydrogen Codes and Standards

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- National Fire Protection Foundation, Quincy, MA
- University of South Carolina Research Foundation, Columbia, SC
- Hawaii Natural Energy Institute at the University of Hawaii, Honolulu, HI
- Smart Chemistry, Sacramento, CA
- Sloane Solutions, Oxford, MI

Project Start Date: 1995

Project End Date: Project continuation and direction determined annually by DOE

Objectives

- Conduct research and development (R&D) needed to establish sound technical requirements for alternative fuel vehicle codes and standards.
- Support code development for the safe use of alternative fuels in transportation applications.
- Advance safety, code development, and market transformation issues through collaborations with appropriate stakeholders.
- Facilitate the safe deployment of alternative fuel technologies.

Technical Barriers

- (A) **Limited Government Influence on Model Codes**
The code development process is voluntary, so the government can affect its progression, but ultimately it is up to the code development organizations (CDOs).
- (B) **Competition among Standards Development Organizations (SDOs) and CDOs**
The competition between various organizations may hinder the creation of consistent vehicle codes and standards.

- (C) **Limited State Funds for New Codes**
Budget shortfalls in many states and local jurisdictions impact the adoption of codes and standards because they do not always have the funds for training building and fire officials.
- (D) **Large Number of Local Government Jurisdictions (approximately 44,000)**
The large number of jurisdictions hinders the universal adoption of codes and standards.
- (E) **Lack of Consistency in Training of Officials**
The training of code officials is not mandated and varies significantly. The large number of jurisdictions leads to variation in training facilities and requirements.
- (F) **Limited DOE Role in the Development of International Standards**
Governments can participate and influence the development of codes and standards, but they cannot direct the development of international standards.
- (G) **Inadequate Representation at International Forums**
Participation in international forums and meetings is voluntary and, to date, has been limited by budgetary constraints.
- (H) **International Competitiveness**
Economic competition complicates the development of international standards.
- (I) **Conflicts between Domestic and International Standards**
National positions can complicate the harmonization of domestic and international standards.
- (J) **Lack of National Consensus on Codes and Standards**
Competitive issues hinder consensus.
- (K) **Lack of Sustained Domestic Industry Support at International Technical Committees**
Cost, time and availability of domestic experts have limited consistent support of the activities conducted within the international technical committees.
- (L) **Competition in Sales of Published Standards**
The development and licensing of codes and standards is a business. The competition among CDOs and SDOs for sales of codes and standards inhibits harmonization of requirements adopted by local jurisdictions.
- (M) **Insufficient Technical Data to Revise Standards**
Research activities are underway to develop and verify the technical data needed to support codes and standards development but are not yet completed.

- (N) **Affordable Insurance is not Available**
New technologies, not yet recognized in codes and standards, will have difficulty in obtaining reasonable insurance.
- (O) **Large Footprint Requirements for Hydrogen Refueling Stations**
The existing set-back distances for siting fueling equipment and other safety requirements result in large footprints.
- (P) **Parking and Other Access Restrictions**
Complete access to parking, tunnels and other travel areas has not yet been secured. Appropriate codes and standards need to be developed to provide safe access to these areas.

Contribution to Achievement of DOE Safety, Codes & Standards Milestones

This project will contribute to achievement of the following Hydrogen Codes and Standards milestone from the DOE Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- **Milestone 21** – Completion of necessary codes and standards needed for the early commercialization and market entry of hydrogen energy technologies. (4Q 2012)

Accomplishments

NREL has accomplished the following in support of the Safety, Codes and Standards section (3.7) of the DOE Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- **Vehicle codes and standards gap analysis:**
Performed an analysis of codes and standards for all six alternative fuel vehicle fuels. The analysis gave background information on the history of fuel usage, the existing codes and standards structure, gaps in the existing codes and standards structure, and research projects or other work needed to fill these codes and standards gaps.
- **Chemical sensor testing and validation:** Began collaborations with key stakeholders; worked on a formal agreement with the European Commission's Joint Research Centre laboratory for testing hydrogen safety sensors; started testing commercially available sensors; participated on International Organization for Standardization (ISO) TC197 WG13 to develop a hydrogen sensor standard.
- **Component testing:** Conducted validation testing of high-pressure onboard hydrogen storage systems; tested hydrogen fueling station breakaways, fittings,

nozzles, and hoses; began work on hydrogen pressure release device (HPRD) testing. This work has been used to develop a HPRD standard by CSA America.

- **Fuel quality specification:** Worked with ISO on technical specification 14687-2; conducted validation testing of particulate measurement methodology; coordinated testing and modeling to understand the effects of contaminants on fuel cell performance.
- **Modeling/simulation of leak scenarios in residential garages:** Completed validation testing at NREL's Thermal Test Facility on full-scale garage model; worked with computational fluid dynamics (CFD) group to develop a modeling/test validation protocol. Published paper in International Journal of Hydrogen Energy describing project and modeling validation.
- **Codes and standards development:** Worked with CDOs and SDOs to develop codes, identify gaps, and provide R&D support; participated on National Hydrogen and Fuel Cell Codes and Standards Coordinating Committee, DOE Codes and Standards Technical Team, and Hydrogen Industry Panel on Codes; assisted DOE Golden Field Office in moving responsibilities for subcontract support to CDOs and SDOs.
- **Codes and standards workshops:** Expanded codes and standards workshops from Fiscal Year 2008 to cover more locations and subject matter. Presented seven workshops in FY 2009 partnering with local fire departments and government organizations.
- **Web-based information compendium:** Released Web-based information compendium as a reference for codes and standards workshop participants and the public; expanding compendium to include other vehicle fuels.

Introduction

It is essential to develop and promulgate codes and standards in order to provide for the safe use of vehicle technologies. With the help of key stakeholders, the DOE Vehicle Technologies Program and NREL are coordinating a collaborative national effort to prepare, review, and promulgate codes and standards for all alternative fuel vehicle technologies.

Approach

The Vehicles Program recognizes that domestic and international codes and standards must be established to enable the timely commercialization and safe use of alternative vehicle fuels. The lack of codes and

standards applicable to vehicle technologies is an institutional barrier to deploying vehicle technologies. It is in the national interest to eliminate this potential barrier. As such, the subprogram works with domestic and international SDOs to facilitate the development of performance-based and prescriptive codes and standards. These standards are then referenced by building and other codes to expedite regulatory approval of vehicle technologies. This approach ensures that U.S. consumers can purchase products that are safe and reliable, regardless of their country of origin, and that U.S. companies can compete internationally.

Results

DOE has identified the 2012 targets for hydrogen safety sensor performance. NREL is testing both commercially available and near-term developmental sensors to identify performance variables relative to the DOE targets. NREL will make their data on sensor testing available through publications or Web access. Fuel quality work at NREL has helped produce a draft ISO fuel quality standard.

NREL has published results of a CFD study on leak scenarios in residential garages. Full-scale experimental validation of the CFD model has been done in NREL's Thermal Test Facility.

To help manage the vehicle safety codes and standards development process, NREL is working directly with key technical committees and at the coordinating committee level. Coordinating Committees include the National Hydrogen and Fuel Cell Codes and Standards Coordinating Committee and DOE's Codes and Standards Technical Team. NREL is also contributing to both national and international standards committees, such as National Fire Protection Association 2, the SAE Fuel Cell Safety Group, and ISO TC 197. With DOE's Golden Field Office, NREL provides support and monitors the progress of work by CDOs and SDOs that is coordinated by Regulatory Logic, LLC.

Facilitating the codes and standards to implement vehicle technologies is a high priority for the program. NREL is continuing work on a DOE initiative to address this need by organizing workshops that include fueling station developers, state and local code officials, and other interested parties. These workshops are targeting regions in which there is project activity. Further work includes developing web based training and educational materials for all six alternative vehicle fuels.

Conclusions and Future Directions

NREL will continue to support the development of codes and standards by:

- Working with DOE and Regulatory Logic to implement a national template for vehicle codes and standards development.
- Continuing R&D support of the key technologies required to close the gaps identified in the codes and standards development process.
- Continuing R&D collaborations with national and international stakeholders on vehicle codes and standards activities.
- Building on coordinating committee efforts to further consolidate and coordinate domestic and international codes and standards activities.

FY 2009 Publications/Presentations

1. C. Rivkin, "US hydrogen Fueling stations: Case Studies" University of Ulster short course in hydrogen safety, 2009.
2. C. Rivkin, C. Blake, R. Burgess, W. Buttner, and M. Post, "Code Compliance Analysis for Indoor Hydrogen Fueling", published in the proceedings of the 2009 National Hydrogen Association meeting.
3. W. Buttner, C. Blake, R. Burgess, M. Post and C. Rivkin. "Development and Compliance to Hydrogen Sensor Codes and Standards the NREL Hydrogen Sensor Testing Laboratory" published in the proceedings of the 2009 National Hydrogen Association meeting.
4. C. Rivkin, C. Blake, R. Burgess, W. Buttner, and M. Post, "CA National Set of Hydrogen Codes and Standards for the US", published in the proceedings of the 2009 International Conference on Hydrogen Safety meeting.
5. W. Buttner, C. Blake, R. Burgess, M. Post and C. Rivkin. "An Overview of Hydrogen Safety Sensors and Requirements" published in the proceedings of the 2009 International Conference on Hydrogen Safety meeting.
6. W. Buttner, R. Burgess, M. Post and C. Rivkin "Hydrogen Sensor Codes and Standards—The NREL Hydrogen Sensor Testing Laboratory," International Energy Association, Experts Meeting Task 19 (invited talk), April 21–24, 2009.
7. W. Buttner, R. Burgess, M. Post and C. Rivkin "An Overview of Hydrogen Sensors and Requirements" IEEE Stationary Battery Meeting (invited talk), June 7–11, 2009.

IX.2 Hydrogen Safety Sensors

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Project Start Date: 2008
Project End Date: 2012 (based on reaching
current multi-year research development and
demonstration plan, safety sensor performance
targets)

Objectives

- Establish testing capabilities to characterize production and near-term development safety sensor performance at mixtures from 0 to 4% hydrogen in air.
- Participate on hydrogen sensor codes and standards development committees.
- Perform testing on hydrogen safety sensors over a range of environmental (e.g., temperature, pressure, relative humidity), chemical (e.g., concentration and composition of interferants) and physical (flow rate, test duration) conditions.
- Develop relationships with manufacturers to facilitate sensor characterization and cultivate the next generation of products capable of meeting DOE performance targets.
- Collaborate with industry and government agencies to develop sensor testing protocols.
- Expand testing capabilities to include 0 to 100% hydrogen concentrations in air.

Technical Barriers

This project addresses the following technical barriers from the Codes and Standards section (3.7.4) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration (RD&D) Plan:

- (A) **Limited Government Influence on Model Codes** – The code development process is voluntary, so the government can affect its progression, but ultimately

it is up to the code development organizations (CDOs).

- (B) **Competition among SDOs and CDOs** – The competition between various organizations hinders the creation of consistent hydrogen codes and standards.
- (C) **Limited State Funds for New Codes** – Budget shortfalls in many states and local jurisdictions impact the adoption of codes and standards because they do not always have the funds for purchasing new codes or for training building and fire officials.
- (F) **Limited DOE Role in the Development of International Standards** – Governments can participate and influence the development of codes and standards, but they cannot direct the development of international standards.
- (G) **Inadequate Representation at International Forums** – Participation in international forums and meetings is voluntary and, to date, has been limited by budgetary constraints.
- (H) **International Competitiveness** – Economic competition complicates the development of international standards.
- (I) **Conflicts between Domestic and International Standards** – National positions can complicate the harmonization of domestic and international standards.
- (J) **Lack of National Consensus on Codes and Standards** – Competitive issues hinder consensus.
- (K) **Lack of Sustained Domestic Industry Support at International Technical Committees** – Cost, time and availability of domestic hydrogen experts have limited consistent support of the activities conducted within the international technical committees.
- (N) **Insufficient Technical Data to Revise Standards** – Research activities are underway to develop and verify the technical data needed to support codes and standards development, retrofitting existing infrastructure and universal parking certification, but are not yet completed.

Contribution to Achievement of DOE Safety, Codes & Standards Milestones

This project will contribute to achievement of the following DOE milestones from the Hydrogen Codes and Standards section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- **Milestone 18:** Implement research program to support new technical committees for the key

standards including fueling interface and fuel storage. (4Q 2007)

- **Milestone 20:** Draft standards for hydrogen detectors in stationary applications (UL). (4Q, 2008)
- **Milestone 21:** Completion of necessary codes and standards needed for the early commercialization and market entry of hydrogen energy technologies. (4Q, 2012)

Accomplishments

- Market definition activities have identified over 120 sensor products to date.
- Test protocols developed to insure reproducible and repeatable testing methodologies.
- Design of new NREL testing chamber and supporting systems. Will provide extended capability and control of operating parameters. Test chamber operational by late Fiscal Year 2009.
- Published sensor lab fact sheet and set up Web-based communication tool for improved flow of time sensitive information.
- Developed collaborations with key stakeholders.

Introduction

Current codes and standards require the use of gas detection for hydrogen installations (example: National Fire Protection Association 52). From response to these requirements, it has become evident that current hydrogen safety sensor products do not always meet the needs of end-users. In April of 2007, a DOE-sponsored hydrogen sensor workshop was held to define end-user needs and formulate these needs into a set of targets for sensor performance. NREL has been tasked with expediting sensor market development in order to meet the DOE multi-year RD&D targets set for 2012.

Approach

By developing standard test methods and measuring sensor performance of a wide range of sensors of different designs and from a many different manufacturers, NREL will characterize the sensor market and identify gaps relative to the DOE targets. With this information we will be able to work closely with sensor manufacturers so that they can better understand the performance of their sensor relative to the needs of hydrogen stationary applications. This work will be directed toward sensor research and development, such that sensor manufacturers, utilizing the resources of a national lab, can expedite their product development life cycle.

In addition, the sensor market expertise gained will be used to support commercialization through development of representative codes and standards for safety sensor certification. Commercialization support will include collaboration with key stakeholders as well as direct participation on the relevant codes and standards committees.

Results

DOE has published performance targets for hydrogen safety sensors in the multi-year RD&D plan (see Table 1). NREL's is working toward characterization of sensor performance relative to the DOE targets by testing commercially available sensors and near-term developmental sensors. Through research on the sensor market, over 120 different sensor technologies have been identified. Information on each of these designs is being compiled in spreadsheet format. This data resource includes manufacturer information, product specifications, contact lists and links to communication logs and test data. The spreadsheet is only available internally. For external communication, manufacturers have access to a Web-based data storage system with password protection. This allows for efficient and secure downloading of manufacturer proprietary data and transfer of larger data files. This Web-based information exchange will also be used for transmitting summary reporting on the sensor testing effort.

NREL is developing standardized test protocols for repeatability and reproducibility of the sensor data. Tests are automated using a LABview data acquisition system. Instrumentation is calibrated with traceability to National Institute of Standards and Technology (NIST) standards. The tests being run are based on emerging standards for safety sensor certification. As an example of the data that is being collected, Figures 1 and 2 show the results of a sample linearity test. This test is run by varying hydrogen gas concentration in air from 0 to 2%. Gas concentration is stepwise increased, recording

TABLE 1. DOE Multi-Year RD&D Targets

Table 3.7.2. Targets for Hydrogen Safety Sensor R&D
<ul style="list-style-type: none"> • Measurement Range: 0.1%-10% • Operating Temperature: -30 to 80°C • Response Time: under one second • Accuracy: 5% of full scale • Gas environment: ambient air, 10%-98% relative humidity range • Lifetime: 10 years • Interference resistant (e.g., hydrocarbons)

FIGURE 1. Sample Sensor Data, 0 to 2% Hydrogen in Air

FIGURE 2. Normalized Hydrogen Sensor Data, 0 to 2% Hydrogen in Air

sensor response at each hold point. Comparing this data to the Table 1 DOE target for measurement range, data show a nonlinear effect near the lower detection limit of 0.1%. This nonlinear effect is most evident on the normalized data plot in Figure 2. Note that the nonlinear sensor response below 0.1% is not necessarily an indication of the lower detection limit. The sensor is continuing to produce a measurable signal that can be corrected through signal processing methods. There is additionally a higher test data variance below 0.1% which would result in degradation in data accuracy.

NREL is in the process of designing and building a new custom test apparatus which will expand the range of environmental condition that the sensors are exposed to. Figure 3 shows the test apparatus during assembly and system check-out testing. The apparatus will be fully operational toward the end of FY 2009. Additional capabilities include a wider temperature range, wider humidity range, vacuum capability and increased number of feed through ports so that an increased number of sensors can be tested concurrently.

For better communication of test project objectives, a sensor lab fact sheet was published and is available

FIGURE 3. NREL's Sensor Test Apparatus

online at www.nrel.gov/hydrogen/pdfs/42987.pdf. There have been several instances where manufacturers have found the fact sheet information online and subsequently contacted NREL to participate in the sensor testing project. In addition to the Web-based communication, NREL is also extending collaboration with national and international organizations working in the area of sensor research and development. This includes codes and standards development organizations such as Underwriters Laboratory (UL) and International Organization for Standardization (ISO) (standards for safety sensor testing include UL2075 and ISO 26142). NREL is collaborating with researchers at NIST's Building and Fire Research Lab working in the area of hydrogen safety sensors. Additionally, the European Commission is supporting hydrogen safety sensor technology with similar program objectives to the DOE/NREL effort. This has resulted in collaboration with the European Commission laboratory Joint Research Centre in Petten Netherlands.

Properly deploying sensors will also require understanding of hydrogen cloud dispersion dynamics thereby insuring sensor installations will accurately detect a hydrogen leak. NREL has recently completed a computational fluid dynamics (CFD) study and test validation of hydrogen gas dispersion in a residential garage. Utilizing this validated model, we can analyze leak scenarios in supporting codes and standards development and also for analyzing specific applications.

Conclusions and Future Directions

NREL will continue supporting the development of improved hydrogen safety sensor products by:

- Working closely with hydrogen safety sensor manufacturers to improve performance, with particular attention to enabling technologies.
- Supporting hydrogen sensor codes and standards development by direct support of codes and standards development organizations.
- Expanding the work on testing protocols through collaboration with key stakeholders.
- Performing a wider range of environmental tests utilizing new NREL test apparatus.
- Integrating CFD leak scenario analysis with sensor project to validate sensor placement.

FY 2009 Publications/Presentations

1. “Test protocol document, hydrogen safety sensor testing. Phase I, Non-flammable mixtures”, R. Burgess, C. Blake, and C. Tracy, NREL/TP-560-42666, NREL Peer reviewed paper.
2. “Low Power MEMS Thermal Conductivity Sensors for H₂ [with discussion of Analog Electronics and Applications]”, B. Balakisanan, W. Buttner, M. Findlay, G. Maclay, J. Stetter, and A. Kelsch, 12th International Meeting on Chemical Sensors, July 2008.
3. “Development and Compliance to Hydrogen Sensor Codes and Standards, The NREL Hydrogen Sensor Testing Laboratory”, R. Burgess et al., NHA Hydrogen Conference, March 2009.
4. “An Overview of Hydrogen Safety Sensors and Requirements”, Buttner et al., 3rd International Conference on Hydrogen Safety (ICHS), to be presented, September 2009.

IX.3 Materials Compatibility

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Project Start Date: FY 2003

Project End Date: Project continuation and
direction determined annually by DOE

Objectives

- (1) Technical Reference on Hydrogen Compatibility of Materials
 - Compile historical data from published technical documents in an Internet-based resource.
 - Update published Technical Reference chapters to reflect new data from current applied research activities.
- (2) Materials Testing
 - Fill gaps in database by generating benchmark data on compatibility of structural materials in hydrogen gas, emphasizing commercial materials tested in high-pressure gas.
 - Establish procedures for generating reliable, conservative design data for structural materials in high-pressure hydrogen gas.
- (3) Codes and Standards Advocacy
 - Participate in the hydrogen codes and standards development/change process.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (D) High Capital Cost and Hydrogen Embrittlement of Pipelines (Section 3.2.4)
- (G) Storage Tank Materials and Costs (Section 3.2.4)
- (N) Insufficient Technical Data to Revise Standards (Section 3.7.4)

Contribution to Achievement of DOE Safety, Codes & Standards Milestones

This project will contribute to achievement of the following DOE milestones from the Codes and Standards section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- **Milestone 6:** Materials compatibility technical reference updated (2Q, 2009). This project directly addresses the milestone by continuing to augment the content of the Technical Reference on Hydrogen Compatibility of Materials, both through the evaluation of published data as well as the generation of new data.
- **Milestone 21:** Completion of necessary codes and standards needed for the early commercialization and market entry of hydrogen energy technologies (4Q, 2012). This project enables the development and implementation of codes and standards by providing expertise and data on hydrogen compatibility of structural materials.

Accomplishments

- Completed new Technical Reference chapters on “stabilized” austenitic stainless steels (i.e., 321 and 347) as well as 2XXX and 7XXX aluminum, increasing the total number of chapters to 21. Updated chapter on duplex stainless steels with data from Sandia materials testing activity.
- Completed measurements of sustained-load cracking thresholds on Ni-Cr-Mo pressure vessel steel American Society of Mechanical Engineers (ASME) SA-372 Grade L in 100 MPa hydrogen gas. These measurements serve as benchmark data for implementing design standards such as ASME Article KD-10.
- Measured cracking thresholds of Cr-Mo pressure vessel steels in 100 MPa hydrogen gas using “crack initiation” test method. Comparison of these “crack initiation” thresholds to the sustained-load cracking thresholds (i.e., “crack arrest” thresholds) indicates that the sustained-load cracking thresholds may be non-conservative.
- Measured fatigue crack growth rates of the Cr-Mo pressure vessel steel ASME SA-372 Grade J in 100 MPa hydrogen gas. These tests represent the successful operation of the new Sandia laboratory capability for measuring fatigue crack growth rates of structural metals in high-pressure hydrogen gas.

Introduction

A major barrier to the development of a hydrogen economy and the deployment of hydrogen technologies is the lack of validated safety codes and standards. The purpose of this project is to provide the technical basis for assessing the safety of hydrogen-based systems with the accumulation of knowledge feeding into the development or modification of relevant codes and standards. The materials compatibility effort focuses on developing a resource entitled the Technical Reference on Hydrogen Compatibility of Materials. This effort is driven by the need for a materials guide, as identified in the Multi-Year Research, Development and Demonstration Plan (Table 3.7.5). The content of the Technical Reference is being developed by identifying and documenting materials data from journal articles and institutional reports. Voids in the database uncovered during the process of composing the Technical Reference are addressed through a materials testing activity.

Approach

The focal point of this Materials Compatibility project is composing the Technical Reference on Hydrogen Compatibility of Materials. To accomplish this objective, two activities are proceeding in parallel: identifying and compiling existing data from technical documents, and generating new data through a materials testing program. The high-priority structural materials featured in these activities are low-alloy and carbon steels, austenitic stainless steels, and aluminum alloys. The materials testing activity emphasizes high hydrogen gas pressures (>100 MPa), fracture mechanics methods, and material fabrication and service variables (e.g., welds, temperature). The data from materials testing are critically reviewed to ensure measurements reflect lower-bound fracture properties and enable structural design.

As part of codes and standards advocacy, Sandia personnel are actively engaged in the codes and standards development process through direct participation in standards development organizations such as ASME, Canadian Standards Association, and International Organization for Standardization. This participation ensures that the standards development organizations have the most current technical information on structural material compatibility. Sandia personnel provide guidance in the development of both component design standards as well as materials testing standards.

Results

Technical Reference

Three new chapters were completed for the electronic, Internet-based version of the Technical Reference, increasing the total number of chapters to 21. These new chapters cover the “stabilized” austenitic stainless steels (i.e., 321 and 347) as well as the 2XXX and 7XXX aluminum alloys. The chapter on 321 and 347 stainless steels was composed in response to needs expressed by stakeholders. The chapters on 2XXX and 7XXX aluminum are the first in the Technical Reference on high-strength aluminum alloys, a technologically important class of alloys that are being considered as lower-cost alternatives to stainless steels in components such as fittings.

Materials Testing

Sustained-load cracking measurements were completed on the Ni-Cr-Mo pressure vessel steel ASME SA-372 Grade L in 100 MPa hydrogen gas. The SA-372 Grade L could be desirable for fabrication of high-pressure hydrogen gas vessels, since the steels can be heat treated more effectively in thick sections. Panels of the SA-372 Grade L were obtained from an industrial partner, who removed the panels from a seamless pipe and heat treated the panels to two different strength levels. One strength level (1,050 MPa yield strength) met the standard specification for SA-372 Grade L steel, while the other strength level (760 MPa yield strength) was substantially reduced to enhance the hydrogen compatibility of the steel. Measurements of the sustained-load cracking thresholds (K_{TH}) are plotted in Figure 1, and the different thresholds for the two strength levels of steel are readily apparent. The lower-strength SA-372 Grade L steel has a K_{TH} value that is similar to the Cr-Mo steel SA-372 Grade J, which was tested previously (Figure 1). Since this Cr-Mo steel is currently used in hydrogen gas pressure vessels, the results suggest that heat treating SA-372 Grade L to a lower strength level could represent a technologically attractive condition for this steel in stationary hydrogen pressure vessels. Similar to previous measurements of K_{TH} for the Cr-Mo pressure vessels steels (Figure 1), measurements for the Ni-Cr-Mo steel SA-372 Grade L are motivated by the materials qualification specifications in ASME Article KD-10.

Fracture toughness tests (i.e., measurements of the threshold for crack propagation under rising displacement) were conducted on the three Cr-Mo pressure vessel steels previously tested under static displacement. The static-displacement procedure is used to measure K_{TH} , where the threshold is defined at crack arrest. In contrast, the fracture toughness tests under rising displacement yield the threshold at crack initiation

FIGURE 1. Benchmark values of K_{IH} measured in 100 MPa hydrogen gas for the Ni-Cr-Mo pressure vessel steel SA-372 Grade L. Included in the plot are previous data measured for Cr-Mo pressure vessel steels in 100 MPa hydrogen gas.

(K_{IH}). The fracture toughness data in 100 MPa hydrogen gas are plotted in Figure 2 to compare these results to the sustained-load cracking thresholds. Figure 2 shows that the fracture toughness and sustained-load cracking measurements are comparable for the highest-strength steel (DOT 3T), but the fracture toughness is notably lower than the sustained-load cracking threshold for the DOT 3AAX and SA-372 Grade J steels. This latter comparison indicates that the “crack arrest” method for measuring the threshold is not the most conservative measurement of crack propagation resistance in hydrogen gas for the lower-strength steels. Since the ASME Article KD-10 currently only requires measurement of the threshold using “crack arrest” methods, these results could lead to consideration of including “crack initiation” (i.e., fracture toughness) measurements as well.

Fatigue crack growth tests in high-pressure hydrogen gas were conducted on three heats of the Cr-Mo pressure vessel steel SA-372 Grade J. The execution of these tests demonstrates the successful effort to develop a capability for conducting fatigue crack growth tests in hydrogen gas up to 100 MPa, and this capability is one of only four known to exist or be in development (the other three are in Japan and the United Kingdom). Fatigue crack growth testing is needed to support the development and implementation of hydrogen containment design codes such as ASME Article KD-10. This code specifies testing to measure fatigue crack growth rates in hydrogen gas to design against fatigue failure, which is promoted by pressure cycling in hydrogen containment components. The fatigue crack growth testing on SA-372 Grade J represents a collaborative effort with an industrial partner. This industrial partner supplied the materials and will use the data (Figure 3) to design a hydrogen gas pressure vessel following ASME Article KD-10.

FIGURE 2. Comparison of fracture toughness values (i.e., “crack initiation” thresholds) to sustained-load cracking thresholds (i.e., “crack arrest” thresholds) for Cr-Mo pressure vessel steels in 100 MPa hydrogen gas.

FIGURE 3. Fatigue crack growth rates measured for three heats of the Cr-Mo pressure vessel steel SA-372 Grade J in 100 MPa hydrogen gas.

Conclusions and Future Directions

- The Technical Reference on Hydrogen Compatibility of Materials continues to evolve as intended, where new chapters are created in response to stakeholder needs and existing chapters are updated to include data generated from the materials testing activity.
- Benchmark sustained-load cracking data that are required to qualify pressure vessel steels for high-

pressure hydrogen service according to ASME Article KD-10 have now been generated for the technologically relevant Ni-Cr-Mo steels as well as the Cr-Mo steels.

- Results showed that the sustained-load cracking threshold (i.e., “crack arrest” threshold) may be non-conservative relative to the fracture toughness (i.e., “crack initiation” threshold) measured in hydrogen gas, which could lead to changes in the test methods in ASME Article KD-10.
 - Fatigue crack propagation rates measured for the Cr-Mo pressure vessel steel ASME SA-372 Grade J in hydrogen represent a rare data set at 100 MPa gas pressure and enable qualification of this steel for high-pressure hydrogen service according to ASME Article KD-10.
 - (future) Create new Technical Reference chapter on nickel alloys and update chapters on ferritic steels with data from materials testing activity.
 - (future) Evaluate the effects of load cycle frequency on fatigue crack growth rate of ferritic steels in hydrogen gas.
 - (future) Compare fatigue crack growth data for stainless steels tested in hydrogen gas vs. hydrogen-precharged condition.
 - (future) Develop reliable methods for measuring fracture response of aluminum alloys in hydrogen gas.
 - (future) Engage domestic and international stakeholders to develop materials qualification standards for pressure manifold components (i.e., fittings, regulators, etc.).
4. (invited presentation) “Variables Affecting Measurement of Sustained Load Cracking Thresholds in Hydrogen Gas”, K. Nibur and B. Somerday, *ISO/TC 58/WG 7 Workshop on H2 Test Methods*, Atlanta, GA, Sept. 2008.
 5. (invited presentation) “Fracture Control of Hydrogen Containment Components”, B. Somerday, *International Hydrogen Energy Development Forum 2009*, Fukuoka, Japan, Feb. 2009.
 6. “Sustained Load Cracking of Steels for Hydrogen Storage and Delivery”, K. Nibur, B. Somerday, D. Balch, and C. San Marchi, in *Effects of Hydrogen on Materials*, ASM International, Materials Park, OH, 2009, in press.
 7. “Hydrogen-Assisted Fracture of Welded AISI 316 Austenitic Stainless Steel”, X. Tang, G. Schiroky, C. San Marchi, and B. Somerday, in *Effects of Hydrogen on Materials*, ASM International, Materials Park, OH, 2009, in press.
 8. “Characterization of Hydrogen-Assisted Fracture Mechanism by Fracture Surface Topography Analysis (FRASTA)”, T. Kobayashi, B. Somerday, C. San Marchi, and K. Nibur, in *Effects of Hydrogen on Materials*, ASM International, Materials Park, OH, 2009, in press.
 9. “Effect of Internal Hydrogen on Fatigue Strength of Type 316 Stainless Steel”, C. Skipper, G. Leisk, A. Saigal, D. Matson, and C. San Marchi, in *Effects of Hydrogen on Materials*, ASM International, Materials Park, OH, 2009, in press.
 10. “Measurement of Fatigue Crack Growth Rates for Steels in Hydrogen Containment Components”, B. Somerday, K. Nibur, and C. San Marchi, submitted to *3rd International Conference on Hydrogen Safety*.

FY 2009 Publications/Presentations

1. *Effects of Hydrogen on Materials: Proceedings of 2008 International Hydrogen Conference*, B. Somerday and P. Sofronis, eds., ASM International, Materials Park, OH, 2009, in press.
2. (invited presentation) “Hydrogen Effects in Materials”, B. Somerday, *3rd European Summer School on Hydrogen Safety*, Belfast, UK, July 2008.
3. (invited presentation) “Hydrogen-Assisted Fracture of Austenitic Stainless Steels”, C. San Marchi et al., *2008 International Hydrogen Conference*, Moran, WY, Sept. 2008.

IX.4 Hydrogen Safety Knowledge Tools

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Project Start Date: March 2003

Project End Date: Project continuation and
direction determined annually by DOE

Objectives

- **Hydrogen Safety Best Practices** - Capture the vast knowledge base of hydrogen experience and make it publicly available. The best practices online manual is a “living” document that provides guidance for ensuring safety in DOE hydrogen projects, while serving as a model for all hydrogen projects and applications.
- **Hydrogen Incident Reporting and Lessons Learned** - Collect information on hydrogen incidents and near-misses and promote widespread sharing of lessons learned, with the goal of preventing similar incidents from occurring in the future.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Safety section of the Hydrogen, Fuel Cells and Infrastructure Technologies (HFCIT) Program Multi-Year Research, Development and Demonstration Plan:

- (A) Limited Historical Database
- (B) Proprietary Data

Contribution to Achievement of DOE Safety, Codes & Standards Milestones

This project will continue to contribute to achievement of DOE Milestone 20 from the Hydrogen Safety section of the HFCIT Program Multi-Year Research, Development and Demonstration Plan:

- **Milestone 20:** Update peer-reviewed Best Practices Handbook. (4Q, 2008)

Related milestones in Task 6 (Hydrogen Safety and Incidents) and Task 7 (Best Practices Handbook) have previously been achieved.

Accomplishments

Hydrogen Safety Best Practices

- We added a section on Laboratory Safety that presents: 1) best practices for designers of laboratories where hydrogen will be used and 2) best practices for researchers who will be working with hydrogen in a laboratory setting. The page on hydride storage and handling was developed by a team led by Sandia National Laboratories (SNL).
- We worked with NASA White Sands Test Facility to create a new page on Vacuum Pumps that covers three pump technologies: positive displacement pumps, momentum transfer pumps, and entrapment pumps.
- We worked with the National Renewable Energy Laboratory to develop a new page on Hydrogen Codes and Standards that provides links to three useful codes and standards Web sites: the American National Standards Institute (ANSI) Hydrogen Codes and Standards Portal [1], the DOE Hydrogen Fueling Stations and Telecommunications Permitting Web site [2], and the Hydrogen/Fuel Cells Codes and Standards Matrix [3].

Hydrogen Incident Reporting and Lessons Learned

- Over the past year, we added 15 new safety event records, for a total of 140 records currently in the database.
- With help from the Hydrogen Safety Panel, we improved the completeness and clarity of the lessons learned text for a number of records.
- We improved the incident submission form and the search function capability to make them more user-friendly.

Introduction

PNNL has developed and continues to improve two software tools to support the Hydrogen Safety Program. This report covers our Hydrogen Safety Best Practices online manual (<http://www.H2BestPractices.org>) and our Hydrogen Incident Reporting and Lessons Learned database (<http://www.H2Incidents.org>). The National Research Council Second Report, *Review of*

the Research Program of the FreedomCAR and Fuel Partnership, states that “The creation of a database on incidents involving hydrogen will be useful in promoting safety.” The report also states that “The committee encourages DOE to continue to develop, publish, and update the best practices document.”

Approach

Hydrogen Safety Best Practices - There are many references and resources that deal with the safe use of hydrogen, and our intent is to organize and compile relevant information in an easy-to-use Web-based manual without duplicating existing resources. PNNL teamed with hydrogen safety experts at the Los Alamos National Laboratory (LANL) and SNL, the Hydrogen Safety Panel, and other subject matter experts to compile, draft, review, and annotate best practices tailored to working with hydrogen.

A best practice is a technique or methodology that has reliably led to a desired result. Using best practices is a commitment to utilizing available knowledge and technology to achieve success. Hydrogen-specific best practices are compiled from a variety of references, and links to Web-based resources and actual PDF files are provided on the Web site.

Hydrogen Incident Reporting and Lessons

Learned - The purpose of H2Incidents.org is to facilitate open sharing of lessons learned from hydrogen safety events to help avoid similar incidents in the future. Our approach to this task included encouraging all DOE-funded projects to submit incidents and near-misses and to provide specific lessons learned. We are pursuing the addition of new records by actively seeking news reports on hydrogen incidents and searching existing databases for hydrogen-related safety event records. We contact private-sector companies who experience hydrogen incidents to solicit their permission to publish incident records. We have established and continue to maintain a mechanism for anonymous submission of records. Specific safety event records are linked to the Best Practices online manual to emphasize safe practices for working with hydrogen and avoiding future incidents. Expert review of all incidents and lessons learned is provided by PNNL staff and the Hydrogen Safety Panel.

Results

Hydrogen Safety Best Practices – PNNL and LANL completed the original sections of the Web site in 2007: Safety Practices (which includes the more management-oriented topics of Safety Culture, Safety Planning, Incident Procedures, and Communications) and Design and Operations (which contains the more engineering-oriented topics of Facility Design Considerations, Storage and Piping, Operating Procedures, and Equipment Maintenance). The

Hydrogen Safety Panel provided initial reviews, followed by a limited public review. The Web site was launched in December 2007 at <http://www.H2BestPractices.org>.

In early 2008, we completed a new section on Laboratory Safety that covers hydrogen-related design and operations elements (ventilation, fume hoods, fire protection, explosion protection, cylinder safety, cryogenic liquid, hydride storage and handling, pressure equipment, leak and flame detection, and emergency plans). The hydride storage and handling section was written by SNL and a team of experts from the International Energy Agency’s Hydrogen Implementing Agreement Task 22, Fundamental and Applied Hydrogen Storage Materials Development. The Laboratory Safety section was published in September 2008, after thorough review by the Hydrogen Safety Panel. The section contains 24 references, with the main one being National Fire Protection Agency 45, “Standard on Fire Protection for Laboratories Using Chemicals”. This past year, we added more downloadable references, more links to related sites, more links to the incident reporting and lessons learned database, and a new hydrogen flame characteristics video that we developed for the DOE Hydrogen Education Program.

Hydrogen Incident Reporting and Lessons

Learned - We added 15 new records to H2Incidents.org during the past year. We now have 140 records in the database, and several more are pending approval by the organizations involved. PNNL staff, the Hydrogen Safety Panel, and others provided technical review of all records, with emphasis on fully capturing lessons learned. A comment submittal feature was added to every page, facilitating direct contact with either the content manager or the webmaster. The URL of the page is automatically attached to the subject line of the e-mail message. The Web site is available at <http://www.H2Incidents.org>.

Conclusions and Future Directions

Hydrogen Safety Best Practices - Our future work includes improving existing Web site content as well as drafting new sections. Some of the improvements we are working on include adding more detail on hydrogen properties, increasing the visibility of management of change, and incorporating additional guidance on outdoor storage of hydrogen cylinders.

Ideas for new content have come from the Hydrogen Safety Panel, other national laboratories with whom we frequently collaborate, technical reviewers at the DOE Annual Merit Review, and actual Web site users. For example, it has been suggested that we should consider the needs of end-user communities with less engineering and technological expertise. In response to this suggestion, we plan to add a new section that is focused on technicians and young engineers with limited

or no knowledge of hydrogen properties and behavior. This new section would be more practical and concise, formatted as a series of simple bullets showing what to do and what not to do, and include lots of photos and graphics.

We will continue to monitor Web site usage and respond to user feedback. Users have submitted many requests for additional information and guidance through the Web site's comment submittal feature. We routinely seek guidance from one or more Hydrogen Safety Panel members in crafting our responses to these requests. We also plan to enhance the Web site utility by continuing to link the content to safety event records in the Hydrogen Incident Reporting and Lessons Learned database and by adding photos, graphics, and videos to complement the text.

Hydrogen Incident Reporting and Lessons

Learned - Our future work will focus on increasing the number of records in the database, partially through identifying additional sources of hydrogen safety event data and lessons learned. A significant part of the effort is expended to work with the national laboratories and private-sector firms that experience hydrogen incidents and/or near-misses to help them communicate what happened, what the primary causes and contributing factors were, and most importantly, what lessons were learned by their organizations that could benefit others if they were freely shared. We are planning to incorporate graphical software to enable the display of the database contents in graphical format. We will continue to monitor website usage and respond to user feedback.

We will also continue to encourage all DOE-funded projects and private-sector organizations to voluntarily submit records of their hydrogen incidents and near-misses. Success requires that people use the incident database and not fear negative consequences from reporting and publicizing safety events. We will continue to maintain confidentiality for the organizations that voluntarily submit incident records and will never attribute specific incidents to any national laboratory or private company.

FY 2009 Publications/Presentations

1. Fassbender, L.L., "Safety Knowledge Tools: Recent Work and Forward Plans," 11th Meeting of the Hydrogen Safety Panel, Washington, D.C., December 10, 2008.
2. *H2 Safety Snapshot*, PNNL-SA-63909, Vol. 1, Issue 1, April 2009. (<http://www.hydrogen.energy.gov/newsletter.html>)
3. Fassbender, L.L., "Hydrogen Safety Knowledge Tools," PNNL-SA-65349, 2009 U.S. DOE Hydrogen Program and Vehicle Technologies Program Review and Peer Evaluation, Arlington, VA, May 22, 2009.
4. Fassbender, L.L., "Hydrogen Safety Best Practices," 12th Meeting of the Hydrogen Safety Panel, Vancouver, B.C., June 23, 2009.
5. Weiner, S.C., LL. Fassbender and K.A. Quick, "Using Hydrogen Safety Best Practices and Learning from Safety Events," PNNL-SA-65427, International Conference on Hydrogen Safety, Ajaccio, Corsica, France, September 16–18, 2009 (manuscript submitted).

References

1. ANSI Hydrogen Codes and Standards Portal (<http://hcsp.us/default.aspx>)
2. DOE Hydrogen Fueling Stations and Telecommunications Permitting Website (<http://www.hydrogen.energy.gov/permitting/>)
3. Hydrogen/Fuel Cells Codes and Standards Matrix (<http://fuelcellstandards.com/>)

IX.5 Hydrogen Fuel Quality

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Project Start Date: October 1, 2006
Project End Date: September 30, 2011

Objectives

- Develop and test new analytical methods for detecting parts-per-billion (ppb) levels of contaminants.
- Employ, modify and/or create novel techniques that allow reproducible measurements of trace level contaminants.
- Test the effects of critical constituents (NH_3 , CO, and H_2S) on fuel cell performance and provide data sets to fuel cell modelers to establish predictive mechanistic models.
- Provide guidance to other test facilities to expedite International Organization for Standardization (ISO) TC197 Working Group 12's experimental results.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Codes and Standards section (3.7) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (I) Conflicts between Domestic and International Standards
- (N) Insufficient Technical Data to Revise Standards

Contribution to Achievement of DOE Codes & Standards Milestones

This project will contribute to achievement of the following DOE milestone from the Codes and Standards sub-program section of the Hydrogen, Fuel Cells

and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- **Milestone 26** - Revised (Society of Automotive Engineers/ISO) hydrogen quality guidelines adopted. (4Q, 2010)

Accomplishments

- Developed new analytical technique for detecting sulfur and verified using environmental scanning electron microscopy.
- Implemented a gravimetric technique to measure electrochemical active surface area of the catalyst.
- Initiated development of an analytical technique for NH_3 analysis.
- Tested critical constituents (NH_3 , CO, and H_2S).
- Developed baseline test procedures for commercial membrane electrode assemblies (MEAs).
- Continued providing data sets to and interacting with fuel cell modelers.

Introduction

LANL scientists have continued their support of the DOE/Energy Efficiency and Renewable Energy Office of Hydrogen, Fuel Cells & Infrastructure Technologies' Safety, Codes and Standards sub-program through their expertise in the various disciplines such as materials physics and applications, chemistry, and modeling. They have maintained a lead role in the collaborative development and implementation of international performance-based codes, standards and regulations based on actual fuel cell performance.

Approach

Our focus on the hydrogen quality emerged from a fuel specification in which the level of the constituents present was based on detection limits. This brings about our two major focus areas: analytical methods development and critical constituent (the most deleterious: NH_3 , CO and H_2S) testing.

We employed commercially available ion selective electrodes to verify the levels of sulfur present in a fuel stream. This proved to be a difficult task considering sulfur has a tendency to stick to most surfaces. In addition, the commercial probes also lacked sensitivity for sulfide ion concentrations below 10^{-5} mole/L (M). However, trace quantities of H_2S may be measured by concentrating the sulfide ion in a solution of sulfide

anti-oxidant buffer if the gas flow time and flow rate are known, together with precise knowledge of the titrant concentration, titrant volume, and volume of sample, provided that isothermal conditions are maintained. Commercial sulfide ion probes may be used as an endpoint indicator for titrations. This method is also being investigated for NH_3 concentration in a solution. However, because of its solubility multiple traps were set-up to enhance this technique. Figures 1 and 2 illustrate the experimental set-up for S and NH_3 .

LANL has continued testing the critical constituents both independently and combined in order to best describe the fuel cell's response as function of the various constituents and the operating condition. Our tests were conducted with 0.1 and 0.2 mg Pt/cm² for the anode and cathode catalyst, respectively. These loadings are consistent with DOE's 2010 technical targets. More recently, the working group members from North America agreed to also test commercial MEAs at 0.1 and 0.4 mg Pt/cm². LANL has developed a set of initial

baseline tests to be performed by the WG-12 members before testing with fuel specification.

Results

We probed the active surface area on several different catalysts using thermal gravimetric analysis (TGA). Two TGA runs were required for analyses: the first was used to clean the surface of the sample and to prepare it for CO adsorption and in the second run, a 1.1% CO in argon mixture was applied to sample and the mass change recorded. Finally, we verified the CO concentration on the sample by gas chromatography analysis. The catalyst samples examined in the first series of experiments were Pt Black (Alfa HiSpec 1000), Pt/ Al_2O_3 (Alfa 5 wt% Pt on gamma alumina), and Pt/XC-72 (ETEK 20 wt% Pt on carbon XC-72). The results are shown in Figure 3 highlight Pt/XC-72 results in which the sample gain approximately 4% after the introduction of CO.

We continued to test NH_3 , CO, and H_2S as isolated contaminants, in addition to testing combinations of these contaminants. Our fuel cell tests were conducted with 0.1 and 0.2 mg Pt/cm² at the anode and cathode electrodes, respectively. We used 50 cm² hardware with Nafion[®] (NRE212) as the membrane and our catalyst was 20% Pt/C (ETEK). In each result shown we operated the cell in constant current mode, 0.8 A/cm², at 80°C with 83% utilization for the hydrogen and 50% for the air. In Figure 4, the fuel cell was exposed to 100 ppb H_2S in the anode feedstream while operating at 100% relative humidity. After approximately 100 hrs of exposure, the voltage dropped by ~70 mV. We noticed a 40 mV increase in voltage 24 hours after returning to pure hydrogen. The voltammogram indicated the presence of S on the electrode surface. In a separate experiment, we tested 1 ppm NH_3 under identical conditions to those mention in the previous experiment. At the end of 100 hrs, the voltage loss was about 40 mV

FIGURE 1. Schematic of S trap using an ISE

FIGURE 2. Experimental Set-Up for NH_3 Trap using Sequential Trapping

FIGURE 3. Weight Change of a Pt/XC-72 Sample after Exposing it to 1.1% CO in Argon

FIGURE 4. Voltage Response to 100 ppb H_2S at 100% Relative Humidity for a Proton Exchange Membrane Fuel Cell with 0.1 and 0.2 mg Pt/cm^2 Operating at 40 A.

FIGURE 5. Voltage and Resistance as a Function of Time after Introducing 1 ppm NH_3 into the Anode Feedstream of a Fuel Cell

as shown in Figure 5. The actual fuel specification call contain multiple contaminants, however through our previous fuel cell testing experience we have identified NH_3 , CO, and H_2S as the constituents having the most impact on fuel cell performance. This is shown in Figure 6, where after less than 70 hours of exposure to 100 ppb CO, 4 ppb H_2S , and 1 ppm NH_3 the voltage loss was 52 mV.

Future Directions

Our technical objectives for Fiscal Year 2009 were achieved. We have agreed to aggressively begin testing commercial MEAs in an attempt to meet the upcoming ISO TC197 deadline. We will also focus on populating the data sheets with high-quality data using

FIGURE 6. Voltage as a Function of Time after Introducing 100 ppb CO, 4 ppb H_2S , and 1 ppm NH_3 into the Anode Feedstream of a Fuel Cell

these commercial MEAs, and further the development of analytical methods for determination of very low concentrations of other contaminants. Next year's objectives:

- Report on results of commercial MEAs at next ISO TC197/WG-12 meeting.
- Optimization of the previously discussed analytical method and its modification for other critical constituents.
- Improve gravimetric capabilities.
- Continue testing the critical constituents (NH_3 , CO, and H_2S) and populating the test matrix.
- Continue providing data sets and interacting with fuel cell modelers.

FY 2009 Publications/Presentations

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2. Eric L. Brosha, Tommy Rockward, Francisco A. Uribe, and Fernando H. Garzon, "Development of Analytical Techniques to Study H_2S Poisoning of PEMFCs and Components", ECS Transactions for 2008 Fuel Cell Seminar and Exposition, Phoenix, AZ, October 2008.
3. C.M. Johnston, H. Xu, E.L. Brosha, J. Chlistunoff, K. More, E. Orler, M. Hawley, and B. Pivovar, "Measurement and Understanding of Catalyst Utilization in Fuel Cells", ECS Transactions for the 214th Meeting of the ECS, Honolulu, HI, October 2008.
4. T. Rockward, I. Urdampilleta, F. Uribe, E.L. Brosha, and F.H. Garzon, "Co-Adsorption Studies of CO and H_2S on Pt Electrodes", ESC Transactions for the 214th Meeting of the ECS, Honolulu, HI, October 2008.

5. Eric L. Brosha, Tommy Rockward, Francisco A. Uribe, and Fernando H. Garzon, "Qualitative Determination of H₂S Crossover Rates in Nafion® Membranes Using Ion-Probe Techniques", ECS Transactions for the 214th Meeting of the ECS, Honolulu, HI, October 2008.
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7. Eric L. Brosha, Rangachary Mukundan, and Fernando H. Garzon, "YSZ-Based Electrochemical Gas Sensors for the Detection of Explosives", ESC Letters 11 (12) J92, 2008.

IX.6 Hydrogen Release Behavior

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Start Date: Fiscal Year 2002

End Date: Project continuation and direction determined annually by DOE

Objectives

- (1) Scenario Analysis, Risk Assessments for Safety
 - Develop a scientific basis and the associated technical data for modifying or developing new codes and standards for the commercial use of hydrogen.
 - Develop benchmark experiments and a defensible analysis strategy for risk assessment of hydrogen systems.
 - Develop and apply risk-informed decision-making tools in the codes and standards development process.
- (2) Hazards Mitigation Technologies for Hydrogen Applications
 - Determine stability and compatibility of candidate odorants with fuel cell components.
- (3) Codes and Standards Advocacy
 - Provide technical program management and support for the Safety, Codes and Standards Program element.
 - Participate in the hydrogen codes and standards development/change process.

Technical Barriers

This project addresses technical barriers from the Codes and Standards section of the Hydrogen, Fuel Cells and Infrastructure Technologies 2007 Multi-Year Research Plan:

- (F) Limited DOE Role in the Development of International Standards

- (I) Conflicts Between Domestic and International Standards
- (N) Insufficient Technical Data to Revise Standards
- (P) Large Footprint Requirements for Hydrogen Fueling Stations
- (Q) Parking and Other Access Restrictions

Contribution to Achievement of DOE Safety, Codes & Standards Milestones

This project contributes to achievement of the following milestones from the Codes and Standards section of the Hydrogen, Fuel Cells and Infrastructure Technologies 2007 Multi-Year Research Development and Demonstration Plan:

- **Milestone 3:** Complete detailed scenario analysis risk assessments. (4Q, 2007)
- **Milestone 4:** Complete analytical experiments and data collection for hydrogen release scenarios as needed to support code development. (2Q, 2008)
- **Milestone 7:** Perform tests of walled hydrogen storage systems. (3Q, 2007)
- **Milestone 21:** Completion of necessary codes and standards needed for the early commercialization and market entry of hydrogen energy technologies (4Q, 2012)

Accomplishments

- Experiments and simulations were completed to characterize the effect of ignition delay time, ignition location, and confinement configuration on the overpressure produced during the ignition of hydrogen leaks near barrier walls.
- A new gaseous hydrogen separation distance table was approved and incorporated into National Fire Protection Association (NFPA) 55. The new table was created by NFPA 2 Task Group 6 based on risk analysis, leak frequency data analysis, and hazard models developed by Sandia.
- Harmonization of consequence models has been achieved for separation distances in International Organization for Standardization (ISO) 20100 and NFPA 55, working through TC197/WG11. Discussions on risk analysis methodology continue.
- The European Union HYdrogen PERmitting (HYPER) project completed the Installation Permitting Guidance for stationary hydrogen and fuel cell systems with contributions by Sandia on barrier wall experiments and models.
- Simulations of pressure relief device (PRD) releases from fuel cell vehicles in tunnels were performed to

determine the evolution of the flammable volume of hydrogen in the tunnel and the over-pressure produced by delayed ignition at different locations.

- Turbulent hydrogen jet ignition and light-up experiments showed that the time-averaged fuel concentration and conventional flammability limits established for quiescent fuel/air mixtures do not correspond to the flammable boundaries of a turbulent hydrogen jet. A predictive model of ignition (flammability factor) of turbulent hydrogen jets was developed and validated with the ignition experiments.
- Princeton University research indicates that auto-ignition is enhanced by blunt-body obstructions due to increases in gas temperature and the promotion of fuel-air mixing.
- Experiments were conducted at the SRI Corral Hollow test site to investigate the effect of electrically charged particles as a source of hydrogen auto-ignition.
- Liquid hydrogen discharge and dispersion models were developed for small (fittings and cracks) and large (choked flow through vents and PRDs) releases.
- Risk assessment tools to support the permitting of hydrogen refueling stations have been developed and will be incorporated on the National Renewable Energy Laboratory (NREL) hydrogen permitting Web site.
- Two candidate odorant molecules were evaluated for fuel cell membrane compatibility and dosing stability by the team of Enersol and the Pennsylvania State University.
- Sandia organized and hosted the spring International Energy Agency (IEA) Task 19 meeting in San Francisco (April 21-23rd). As participants in IEA Task 19 hydrogen safety, we have generated written guidance on risk criteria and harm criteria.

Introduction

The purpose of this comprehensive project is to enable risk-informed development of codes and standards for hydrogen fuel cell technology that is based on a traceable, scientific foundation. Our scenario analysis and risk assessment efforts focus on defining scenarios for the unintended release of hydrogen and quantifying the consequences through scientific experimentation and modeling. Quantitative risk assessment (QRA) is used to identify risk drivers and risk mitigation strategies for the commercial use of hydrogen. We combine our validated models with QRA to support risk-informed decision-making in the code development process.

Approach

A significant number of tasks are focused on combustion behavior and thermal effects from the unintended release of hydrogen in the built environment, namely barrier wall interactions, ignition characteristics, partially confined spaces (tunnels, garages, warehouses), and liquid hydrogen handling. Technical information is used by codes and standards developers writing for International Code Council and NFPA, also through the Hydrogen Industry Panel on Codes. International partnerships for vetting technical data and analysis methods occur through activities such as IEA Task 19 on Hydrogen Safety and the European HYPER project. Recent work has focused on harmonizing separation distance approaches for ISO 20100, hydrogen fueling.

Results

Risk Assessment: QRA was used to help establish risk-informed separation distances in ISO 20100 for gaseous hydrogen refueling stations through TC197/WG11. To support the ISO and IEA Task 19 (hydrogen safety) efforts, risk criteria and harm criteria were surveyed and adopted values were documented. Additional QRA analyses continued this year focusing on the risk tradeoffs associated with the use of barriers to protect the public and facilities from hydrogen jet fires. A joint effort with NREL to establish Web-based risk assessment tools also continued this year.

Barrier Wall Design: Experiments and simulations were completed to characterize the effect of ignition delay time, ignition location, and barrier wall configuration on the over-pressure produced during the ignition of hydrogen leaks. In addition to single-wall and three-sided wall (135° wall angles) barriers, a new configuration consisting of three-walls with a 90° wall angle was evaluated, shown in Figure 1. The experimental ignition delay time was varied between 67 msec and 6 seconds after leak initiation. The over-pressure remains nearly constant over the range of delay times with all three-wall configurations. This general behavior agrees with our models. Numerical simulations with FLACS (FLame ACceleration Simulator) show that barrier walls reduce the lateral and vertical extent of hazard distances by approximately 50% as compared to a free jet. Because safety distances in the new NFPA 55 table are based on these same pressures and leak diameters of our simulations, model results indicate that use of a barrier wall would allow the reduction of safety distances by approximately half.

Partially Enclosed Spaces: Simulations of releases from hydrogen fuel cell vehicle tanks in tunnels were performed to understand potential over-pressures from delayed ignition of a PRD release, most likely due to a vehicle fire. Dispersion of ignitable clouds of hydrogen following the blow-down of 70 MPa gaseous

tanks through a PRD was determined for transversely and longitudinally ventilated tunnels over a range of operating conditions. Transient simulation of the ignition of the flammable cloud was used to estimate deflagration overpressure. Results indicate that ignition overpressure is sensitive to ignition delay time and position, with the lower overpressures occurring for short ignition delay times (approximately <2 sec) when the flammable volume is rich or for longer ignition delay times (approximately >10 sec) where the flammable volume has dispersed to a lean concentration. These delays are the most likely ignition scenarios because the mixture will ignite early near the fire that actuates the PRD or away from the vehicle at some other ignition source.

FIGURE 1. Variation in overpressure with ignition delay time for single-wall, three-sided wall with 135° angle, and three-sided wall with 90° angle (pressure transducer located in front of wall).

Lean Ignition Limits in Turbulent Jets: Previous experience shows that the lower flammability limits for a quiescent hydrogen mixture do not match mean values for highly fluctuating, turbulent jets. The probability of ignition (P_i) of turbulent hydrogen jets into air was determined using a pulsed Nd:YAG laser, focused to generate an ignition spark that served as the ignition source. Laser Rayleigh scattering was used to characterize the fuel concentration throughout the jet. The dramatic differences between the time-averaged hydrogen concentration field and the instantaneous field give clues to why the average concentration and conventional flammability limits established for quiescent fuel/air mixtures do not correspond to the flammable boundaries of turbulent fuel jets. The measured hydrogen jet light-up contour is shown in Figure 2. Local ignition could only be obtained if the instantaneous composition at the ignition point was within the static flammability limits. In addition to the direct measurement of P_i , the measured probability distribution functions of local fuel concentration were integrated over the static flammability limits to obtain the measured flammability factor, which provides a good representation of P_i . Models of P_i were developed and validated by comparing with measured flammability

FIGURE 2. Jet light-up contours for the H_2 jet. Each point is the mean of five tests.

factors. Validated models can be used to provide a technical basis for the determination of safety distances in codes and standards regulations for flammable gases.

Auto-Ignition Mechanisms: The ignition source in many reported incidents has not been identified, often referred to as an auto-ignition event. Two of the most likely ignition sources for these events include shock heating of the resulting hydrogen/air mixture and ignition due to electrostatically charged particles. In collaboration with Princeton University, we implemented a combined experimental and modeling program to identify the potential role of shock heating as an auto-ignition source. Princeton research indicates that auto-ignition is enhanced by blunt-body obstructions due to increases in gas temperature and the promotion of fuel-air mixing. We worked with SRI to study electrically charged particles as a source of auto-ignition. Experiments conducted at the Corral Hollow test site focused on determining what factors create the highest particle charges in hydrogen flow through pipes and an investigation of whether a static discharge in such a flow can cause auto-ignition. It was found that the highest charge was detected when the particles passed through a 10-foot steel pipe prior to exiting the nozzle. A grounded probe was placed in the charged particle stream in an attempt to achieve auto-ignition. Five attempts were made to ignite the hydrogen jet by discharging the charge particle cloud to the grounded probe, but no successful ignitions were achieved.

Liquid Hydrogen: A series of computer models were developed to describe the behavior of hydrogen as it is being discharged from a liquid hydrogen storage system. The models account for discharge from both the saturated liquid and saturated vapor portions of the hydrogen storage system. Models were developed for slow leaks with large pressure drops like those typically occurring from fittings or small cracks. Models were also developed for larger choked flow discharges like those that might occur from pressure relief devices, vent stacks, or the intentional discharge of hydrogen during fuel transfer. Validation for high-momentum cold hydrogen jets was accomplished by comparing predictions for centerline hydrogen concentration with those measured by Forschungszentrum Karlsruhe.

Odorants: Two candidate molecules were investigated as odorants for hydrogen gas by the team of Enersol and the Pennsylvania State University. It was found that molecule A had no adverse effect on the polarization and long term (16 hr) degradation up to 40 ppm in concentration. At higher concentrations of molecule A (400 ppm), fuel cell performance degraded. For molecule B, the extent of degradation in the long-term fuel cell performance depended on the concentration with no negative impacts on performance at concentrations up to 30 ppm. The performance degradation was found to be completely reversible by feeding pure hydrogen.

Conclusions and Future Directions

- Barrier walls can be used to reduce setbacks by factor of two.
- No ignition-timing versus over-pressure sensitivities were observed for jet flow obstructed by barrier walls.
- The cryogenic vapor cloud model indicates hazard length scales exceed the room-temperature release; validation experiments are required to confirm.
- Light-up maps have been developed for lean-limit ignition; flammability factor model provides a good indication of ignition probability.
- (future) Hydrogen ignition experiments will be conducted in turbulent jet flows that interact with surfaces to provide data for ignition model validation in more complex flow environments. Risk-informed separation distances will be updated with new ignition probabilities.
- (future) Lab-scale cryogenic vapor experiments will be conducted for low-momentum jets to provide validation data. Validated cryogenic leak models will be used to predict flammability envelopes for credible release scenarios
- (future) Validation experiments for hydrogen releases in partially-confined enclosures such as tunnels and parking structures will be performed. The risk associated with accidental releases of hydrogen in tunnels, parking structures, and storage sheds will be evaluated.

FY 2009 Publications/Presentations

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8. Winters, "Modeling Vessel Fillup and Blowdown," SAND 2009-0100.

9. Diop, et al., "A Parametric Study of Jet-Wall Interactions for Compressed Hydrogen Gas Leak Scenarios," 42nd AIAA Aerospace Sciences Meeting, January 2009.
10. Houf, Evans, and Schefer, "Analysis of Jet Flames and Unignited Jets from Unintended Releases of Hydrogen," *Int. J. Hydrogen Energy*, February 2009.
11. Schefer, et al., "Experimental Evaluation of Barrier Walls for Risk Reduction of Unintended Hydrogen Releases," *Int. J. Hydrogen Energy*, Vol. 34, February 2009.
12. LaChance, Houf, Middleton and Fluer, "Analyses to support development of risk-informed separation distances for hydrogen codes and standards," SAND2009-0874.
13. Houf, et al. "Evaluation of Barrier Walls for Mitigation of Unintended Releases of Hydrogen," 2009 NHA Conference.
14. LaChance, et al. "Development of Uniform Harm Criteria for Use in the Quantitative Risk Analysis of the Hydrogen Infrastructure," 2009 NHA Conference
15. Winters and Houf, "Results from an Analytical Investigation of Small-Scale Releases from Liquid Hydrogen Storage Systems," 2009 NHA Conference.
16. Sprague, et al., "Odorization of Hydrogen for Fuel Leak Detection," 2009 NHA.
17. Zhang, Ruggles, and Schefer, "Ignitability limits for combustion of hydrogen in turbulent flows," Sixth U.S. National Combustion Mtg., Ann Arbor, MI, May 2009.
18. Winters and Houf, NHA Fuel Cell Safety Report, May 2009.
19. Lee, et al., "Impact of Hydrogen Odorants on PEMFC Performance," 215th Electro. Chem. Soc Mtg, San Francisco, CA, May 2009.
20. Houf, et al., "Evaluation of Barrier Walls for Mitigation of Unintended Releases of Hydrogen," NHA Online Fuel Cell Safety Report, May 2009.
21. Twelve stakeholder briefings throughout FY 2009.

IX.7 Hydrogen Safety Panel

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- Don Frikken, Becht Engineering, St. Louis, MO
- Richard A. Kallman, City of Santa Fe Springs, CA
- Michael Pero, Hydrogen Safety, LLC, Newington, CT
- Glenn W. Scheffler, GWS Solutions of Tolland, LLC, Tolland, CT
- Andrew J. Sherman, Powdermet Inc., Euclid, OH
- Ian Sutherland, General Motors, Warren, MI
- Edward G. Skolnik, Energetics, Inc. Columbia, MD
- Robert G. Zalosh, Firexplo, Worcester, MA

Project Start Date: Fiscal Year 2004
Project End Date: Project continuation and direction determined annually in consultation with DOE

Objectives

- Provide expertise and guidance to DOE and assist with identifying safety-related technical data gaps, best practices and lessons learned.
- Help DOE integrate safety planning into funded projects to ensure that all projects address and incorporate hydrogen and related safety practices.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Safety section (3.8) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) Limited Historical Database
- (B) Proprietary Data
- (C) Validity Of Historical Data
- (D) Liability Issues
- (E) Variation in Standard Practice of Safety Assessments for Components and Energy Systems

- (F) Safety is not Always Treated as a Continuous Process
- (G) Expense of Data Collection and Maintenance
- (H) Lack of Hydrogen Knowledge by Authorities Having Jurisdiction
- (I) Lack of Hydrogen Training Facilities for Emergency Responders

Contribution to Achievement of DOE Hydrogen Safety Milestones

This project will contribute to achievement of the following DOE milestones from the Hydrogen Safety section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- **Milestone 8:** Complete investigation of safe refueling protocols for high pressure systems. (1Q, 2012)
- **Milestone 12:** Complete research needed to fill data gaps on hydrogen properties and behaviors. (2Q, 2010)
- **Milestone 20:** Update peer-reviewed Best Practices Handbook (4Q, 2008)

Related milestones in Task 5 (Safety of DOE R&D Projects), Task 6 (Hydrogen Safety and Incidents), Task 7 (Best Practices Handbook) and Task 8 (Hydrogen Safety Props) of the above reference have all been achieved with support from the Hydrogen Safety Panel.

Accomplishments

- Conducted two meetings of the Hydrogen Safety Panel: December 10–11, 2008, Energetics, Inc., Washington, DC; June 23–25, 2009, Powertech Labs/Ballard Power Systems, Vancouver, BC.
- Conducted seven safety reviews for projects in hydrogen storage, fuel cells and production and delivery and submitted reports to DOE per established protocol.
- Reviewed 50 safety plans since July 1, 2008 for projects in hydrogen storage, fuel cells, production and delivery and manufacturing utilizing DOE/ Panel-prepared safety planning guidance [1].
- Provided technical guidance, source material and review for the Hydrogen Incident Reporting and Lessons Learned Database (www.h2incidents.org), the Hydrogen Safety Best Practices Web site (www.h2bestpractices.org) and *H2 Safety Snapshot*, a new topical safety bulletin [2].

- Completed *Secondary Protection for 70 MPa Fueling, A White Paper from the Hydrogen Safety Panel* with recommendations to DOE regarding fueling a vehicle equipped with a lower-service-pressure fuel tank from a higher-pressure fueling source [3].

Introduction

Safety is an essential element for realizing the “hydrogen economy” – safe operation in all of its aspects from hydrogen production through storage, distribution and use; from research, development and demonstration to commercialization. As such, safety is given paramount importance in all facets of the research, development and demonstration of the U.S. DOE Hydrogen, Fuel Cells and Infrastructure Technologies Program Office.

Recognizing the nature of the DOE program and the importance of safety planning, the Hydrogen Safety Panel was formed in December 2003 to bring a broad cross-section of expertise from the industrial, government and academic sectors to help ensure the success of the program as a whole. The experience of the Panel resides in industrial hydrogen production and supply, hydrogen research and development and applications, process safety and engineering, materials technology, industrial liability and facility insurance, risk analysis, accident investigation and fire protection. The Panel provides expertise and guidance on safety-related issues and technical data gaps, reviews individual DOE-supported projects and their safety plans and explores ways to bring best practices and lessons learned to broadly benefit the DOE program.

Approach

The Panel strives to raise safety consciousness most directly at the project level. Safety should be driven at the project level by organizational policies and procedures, safety culture and priority. Project safety plans are reviewed in order to encourage thorough and continuous attention to safety aspects of the specific work being conducted. Panel-conducted safety reviews focus on engagement, learning, knowledge-sharing and active discussion of safety practices and lessons learned, rather than as audits or regulatory exercises. Through this approach, DOE and the Hydrogen Safety Panel are trying to achieve safe operation, handling and use of hydrogen and hydrogen systems for all DOE projects.

Results

The Hydrogen Safety Panel was formed in FY 2004 and the first meeting was held in Washington, D.C.,

December 11–12, 2003. The Panel conducted its 11th and 12th meetings in FY 2009 as noted above. Current Panel membership is noted in Table 1.

TABLE 1. Hydrogen Safety Panel

Richard A. Kallman, Chair	City of Santa Fe Springs, CA
Steven C. Weiner, Program Manager	PNNL
Addison Bain	NASA (ret)
Harold Beeson	NASA White Sands Test Facility
David J. Farese	Air Products and Chemicals, Inc.
Don Frikken	Becht Engineering
Michael Pero	Hydrogen Safety, LLC
Harold L. Phillippi	ExxonMobil Research and Engineering
Glenn W. Scheffler	GWS Solutions of Tolland, LLC
Andrew J. Sherman	Powdermet Inc.
Ian Sutherland	General Motors
Robert G. Zalosh	Firexplo
Nicholas F. Barilo, Technical Support	PNNL
Edward G. Skolnik, Technical Support	Energetics, Inc.

The Panel conducted safety reviews for the projects noted in Table 2 since the last reporting (37 such safety reviews have been conducted since March 2004). Preliminary reports have been issued for all these safety reviews and the completed final report with recommendations is referenced in Table 2. Final reports were also issued for safety reviews previously conducted [5,6].

In addition to reviewing safety plans, the Panel commended two additional safety plans to DOE as “good examples” for their reference and use: (1) “Safe Detector System for Hydrogen Leaks” (Intelligent Optical Systems, Inc.) and (2) “Renewable and Logistics Fuels for Fuel Cells (Colorado School of Mines). Six such safety plans have now been commended to DOE for those purposes.

The Panel considered the issue of fueling a vehicle equipped with a lower-service-pressure fuel tank from a higher-pressure fueling source. Recognizing that filling a lower-service-pressure vehicle at a 70 MPa fueling source is likely to result in a catastrophic event, a white paper (*Secondary Protection for 70 MPa Fueling, A White Paper from the Hydrogen Safety Panel*) with recommendations was prepared and submitted to DOE [3].

Several Panel members contributed to a National Fire Protection Association (NFPA) study undertaken in 2008-2009 to identify and evaluate the research needed to support the development of hydrogen safety requirements in NFPA codes and to make recommendations on research programs needed

TABLE 2. Hydrogen Project Safety Reviews Since July 1, 2008

Program Area	Project Title	Contractor
Fuel Cells	Fuel Cell Testing at Argonne National Laboratory	Argonne National Laboratory, Argonne, IL
Fuel Cells	Development of a Novel Efficient Solid-Oxide Hybrid for Co-Generation of Hydrogen and Electricity Using Nearby Resources for Local Applications* [4]	Materials and Systems Research, Inc., Salt Lake City, UT
Fuel Cells,	High Temperature, Low Relative Humidity Membrane Program	University of Central Florida, Cocoa, FL
Production and Delivery	Investigation of Reaction Networks and Active Sites in Bio-Ethanol Steam Reforming over Co-based Catalysts	Ohio State University, Columbus, OH
Production and Delivery	Carbon Molecular Sieve Membrane as Reactor/Separator for Water Gas Shift Reaction	Media and Process Technology Inc., Pittsburgh, PA
Production and Delivery	Materials Solutions for Hydrogen Delivery in Pipelines	Secat, Inc., Lexington, KY

*conducted as both a telephone interview and a site visit

to support these code changes [7]. The Panel also supported the incident investigation of the fire that occurred at the Shell Hydrogen refueling station, White Plains, NY in August 2008 [8].

Conclusions and Future Directions

Being conscious of the need to use safe practices is a necessary first step for the conduct of all work. The work and approaches taken by the Panel will continue to focus on how safety knowledge, practices and lessons learned can be brought to bear on the safe conduct of project work.

In addition to continuing to review project safety plans and conduct safety review site visits for selected projects, the Panel will undertake a number of initiatives including:

- Conduct follow-up teleconferences with project teams for which safety review site visit reports have been issued since 2007 in order to identify actions taken, conclusions, findings and learnings.
- Select topics for future issues of *H2 Safety Snapshot* and serve in an advisory capacity for publication.
- Consider additional topics for study consistent with the Hydrogen Safety Panel's charter to identify safety-related data and knowledge gaps.

The 13th and 14th meetings of the Hydrogen Safety Panel are planned for December 2009 and June 2010, respectively.

FY 2009 Publications/Presentations

1. Weiner, S.C. and Barilo, N.F., "Hydrogen Safety Panel: Shaping Safety Awareness and Practice," PNNL-SA-61902, 2008 Mary Kay O'Connor Process Safety Center International Symposium, College Station, TX, October 28–29, 2008. (<http://psc.tamu.edu/symposia/2008/symposium-program>)
2. Hoagland, W., Tchouvelev, A.V., Versloot, N.H.A. and S.C. Weiner, "Technology Spotlight: Task 19 Hydrogen Safety," IEA HIA Newsletter, Vol. 2, No. 2, November 2008. (<http://www.ieahia.org/page.php?s=glance&p=news>)
3. Weiner S.C., "Hydrogen Safety Panel," PNNL-SA-65397, DOE Hydrogen Program and Vehicle Technologies Program Review, Arlington, VA, May 22, 2009. (http://www1.eere.energy.gov/vehiclesandfuels/resources/proceedings/2009_merit_review.html)
4. Weiner, S.C., Fassbender, L.L. and K.A. Quick, "Using Hydrogen Safety Best Practices and Learning from Safety Events," PNNL-SA-65427, International Conference on Hydrogen Safety, Ajaccio, Corsica, France, September 16–18, 2009.
5. Zalosh, R.G. and N.F. Barilo, "Wide Area and Distributed Hydrogen Sensors," PNNL-SA-65498, International Conference on Hydrogen Safety, Ajaccio, Corsica, France, September 16–18, 2009.
6. Weiner, S.C., R.A. Kallman and E.G. Skolnik, "Speaking of Safety: Learning from Safety Reviews," PNNL-SA-66356, 18th World Hydrogen Energy Conference, Essen, Germany, May 16–21, 2010. (abstract submitted)

References

1. "Safety Planning Guidance for Hydrogen Projects, November 2007," U.S. Department of Energy, Hydrogen, Fuel Cells & Infrastructure Technologies Program Office. (<http://www1.eere.energy.gov/hydrogenandfuelcells/codes/oversight.html>)
2. *H2 Safety Snapshot*, PNNL-SA-63909, Vol. 1, Issue 1, April 2009. (<http://www.hydrogen.energy.gov/newsletter.html>)
3. *Secondary Protection for 70 MPa Fueling, A White Paper from the Hydrogen Safety Panel*, PNNL-18523, July 6, 2009.
4. Barilo, N.F., Frikken, D., Skolnik, E.G. and S.C. Weiner, "Safety Evaluation Report: Development of a Novel Efficient Solid-Oxide Hybrid for Co-Generation of Hydrogen and Electricity Using Nearby resources for Local Applications, MSRI, Salt Lake City, UT," PNNL-18570, July 16, 2009.
5. Bain, A., Frikken, D., Skolnik, E.G. and S.C. Weiner, "Safety Evaluation Report: Controlled Hydrogen Fleet and Infrastructure Demonstration and Validation Project, Hydrogen Fueling Station, Oakland, CA," PNNL-17685, July 25, 2008.
6. Bain, A., Zalosh, R.G., Skolnik, E.G. and S.C. Weiner, "Safety Evaluation Report: Controlled Hydrogen Fleet and

Infrastructure Demonstration and Validation Project, Shell Hydrogen Refueling Station, Washington, DC,” PNNL-18191, January 27, 2009.

7. “Research Needs in Support of Hydrogen Safety Standards,” Hydrogen Research Advisory Council (R.G. Zalosh, chair), Fire Protection Research Foundation, National Fire Protection Association, 2009.

8. Sell, R.B., “Hydrogen Vehicle and Infrastructure Demonstration and Validation,” DOE Hydrogen Program and Vehicle Technologies Program Review, Arlington, VA, May 20, 2009.

IX.8 Codes & Standards for the Hydrogen Economy

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Contract Number: DE-FC36-07GO17004

Subcontractors:

- American National Standards Institute (ANSI), New York, NY
- Compressed Gas Association (CGA), Inc., Chantilly, VA
- CSA America, Cleveland, OH
- GWS Solutions of Tolland, Tolland, CT
- United States Fuel Cell Council (USFCC), Washington, D.C.
- International Code Council, Inc., Country Club Hills, IL
- Kelvin Hecht, Avon, CT
- National Hydrogen Association, Washington, D.C.
- National Fire Protection Association (NFPA), Quincy, MA
- Society of Automotive Engineers (SAE) International, Troy, MI
- FP2 (Martin T Gresho, PE), Livermore, CA
- James M. Ohi, PhD, Denver, CO

Project Start Date: December 5, 2006

Project End Date: September 30, 2011

Objectives

- Develop a supporting research and development project to provide critical hydrogen behavior data and a detailed understanding of hydrogen combustion and safety across a range of scenarios which are needed to establish setback distances in building codes and minimize the overall data gaps in code development.
- Support and facilitate the effort, led by the NFPA, to complete the draft Hydrogen Technologies Code (NFPA 2).
- With experimental data and input from Technology Validation subprogram element activities, support and facilitate the completion of standards for bulk hydrogen storage (e.g., NFPA 55).
- Facilitate the adoption of the most recently available model codes (e.g., from the International Code Council [ICC]) in key regions.
- Complete preliminary research and development on hydrogen release scenarios to support the establishment of setback distances in building codes and provide a sound basis for model code development and adoption.
- Support and facilitate the development of Global Technical Regulations (GTR) by 2010 for hydrogen vehicle systems under the United Nations Economic Commission for Europe, World Forum for Harmonization of Vehicle Regulations and Working Party on Pollution and Energy Program (ECE-WP29/GRPE).
- Support and facilitate the completion by 2012 of necessary codes and standards needed for the early commercialization and market entry of hydrogen energy technologies.

Technical Barriers

This project addresses the following technical barriers from the Codes & Standards section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) Limited Government Influence on Model Codes
- (B) Competition among SDOs and CDOs
- (C) Limited State Funds for New Codes
- (D) Large Number of Local Government Jurisdictions (approximately 44,000)
- (E) Lack of Consistency in Training of Officials
- (F) Limited DOE Role in the Development of International Standards
- (G) Inadequate Representation at International Forums
- (H) International Competitiveness
- (I) Conflicts between Domestic and International Standards
- (J) Lack of National Consensus on Codes and Standards
- (K) Lack of Sustained Domestic Industry Support at International Technical Committees
- (L) Competition in Sales of Published Standards
- (M) Jurisdictional Legacy Issues
- (N) Insufficient Technical Data to Revise Standards
- (O) Affordable Insurance is Not Available

- (P) Large Footprint Requirements for Hydrogen Refueling Stations
- (Q) Parking and Other Access Restrictions

Accomplishments

NFPA: Entered NFPA 2 into the Fall 2010 Revision Cycle; released draft of NFPA 2, Hydrogen Technologies Code, now ready for public proposals.

Glenn Scheffler: Supported the U.S. delegation in the drafting of the GTR for fuel cell vehicles (FCVs); chaired the SAE Safety Working Group; wrote and presented a paper of FCV Safety at the 2009 SAE World Congress; chaired the U.S. Technical Advisory Groups (USTAGs) for both ISO TC197 for hydrogen and TC22/SC21 for electric vehicles including FCVs.

USFCC: Served as chair of the Technologies Committee which is responsible for development of NFPA 2 (see NFPA, above); completed first formal technical meeting focused on addressing all public proposals received during the solicitation period; changed technical committee membership representation from Sandia Labs to FP2 (Marty Gresho, another Regulatory Logic subcontractor funded by DOE) to address concerns related to separation of code makers from researchers; selected new alternate member. (Approval anticipated August 2009.)

NFPA 55 Compressed Gas Standard - Separation distance proposal developed, submitted and approved; NFPA 51A Report On Proposals meeting completed; Hydrogen Industry Panel on Codes (HIPOC) participation included development of several code change proposals to the International Fire Code (IFC) for HIPOC review, deliberation and approval; started NFPA 52 versus IFC Chapter 22 review to identify additional correlating code change proposals needed; supported NFPA 52 motion to NFPA general assembly and appeal to NFPA Standards Council with coordinated in- person appearances and testimony; initiated reformulation of HIPOC charter to balance membership and scope.

NHA: Expanded Hydrogen and Fuel Cell Safety Report to include regular contributions by the USFCC and others; developed a primer for parties who are new to hydrogen and fuel cell codes and standards; conducted a codes and standards workshop in conjunction with the NHA Annual Conference in March 2009; published reports on key national codes activities and international standards activities between NFPA's Hydrogen Technology Technical Committee (NFPA 2) and NFPA's Industrial and Medical standards activities to keep interested parties informed and provide opportunities for comment; played a leading role in developing administrative procedures for the HIPOC for 2009.

CGA: A joint task group effort was undertaken by the Gases Technical Committee to establish scientifically based fundamental separation distances between bulk compressed hydrogen systems and sensitive receptors ("exposures"). Distances are designated as "fundamental" to indicate that these distances may be altered with the application of mitigation methods, some of which have been identified while others remain in the developmental phase

SAE: Completed two research projects, thereby establishing sound technical requirements for hydrogen codes and standards; published three Technical Information Reports advancing hydrogen safety standards and code development

Kelvin Hecht: Completed redesign of the American National Standards Institute (ANSI) portal (supported by ANSI, another Regulatory Logic subcontractor) in response to National Renewable Energy Laboratory suggestions, with limited impact on users; continued to monitor the status of approximately 150 U.S. and 80 international standards, and to update the Web site in real time when changes in standards occur; provided a valuable resource to hydrogen and fuel cell development efforts and to authorities having jurisdiction for siting and operating permits as demonstrated by almost 6,000 visits per month, as well as disseminating knowledge to researchers and graduate students as reference material to address development of commercial hydrogen energy resources.

Introduction

As suggested by the barriers listed previously, the Codes & Standards area is an unusual DOE activity in that the ultimate goals and objectives cannot be achieved directly by DOE or its contractors, but must be met indirectly, as the necessary process of consensus-based codes and standards development is carried out. Virtually all relevant hydrogen-related codes and standards work rests on a voluntary, consensus-based process, in contrast to the direct development of government-based rules and regulations. In addressing the barriers, therefore, this project relies on positioning the strategic value of targeted resources aimed at removing identified "log jams" in the process, and the provision of resources when the voluntary process would otherwise succumb to delays inherent in such negotiated results. This approach enhances the free flow of important and credible information, including supporting research wherever necessary to develop or adapt new codes and standards, consistently supporting optimum participation by U.S. industry and related industry associations.

Approach

This project utilizes close collaboration between DOE program leadership, national laboratory technical experts, and the individual standards development organization (SDO) and code development organization (CDO) sub-awardees to identify the highest value contributions available for improving timeliness of the consensus-based standard development process for successful commercialization of hydrogen in stationary and mobile applications.

Results

See also the achievements listed previously: The major achievement for the year has been that NFPA 2 has been issued and entered into the standard cycle – this is a major milestone from many perspectives, including establishment of scientifically-based fundamental separation distances between bulk compressed hydrogen systems and sensitive receptors (“exposures”).

Conclusions and Future Directions

Regulatory Logic’s close collaboration with DOE and the technical experts of the national laboratories continues the funding announcement prescription that the awardee work in close collaboration with DOE to fulfill objectives of the project. The subcontractors contributing to the NFPA 2 portion of the project will continue to support and improve this document during the development cycle; subcontractors, including NHA, USFCC, ICC, SAE, ANSI, NFPA, and CSA America shall continue to publish articles and announcements of interest to the hydrogen and fuel cell communities from USFCC and third parties. In addition to expanding the reach of available information, this effort reduces the cost of producing the Hydrogen and Fuel Cell Safety Reports, as fewer original articles will need to be written due to harmonization efforts by subcontractors. The Hydrogen Primer will be included posted under the “Technical Resources” area of the Hydrogen and

Fuel Cell Safety Web site to make it easy for interested parties to locate. This tool is additionally useful for presentations to countries which are just beginning to establish national codes and standards for hydrogen and fuel cell systems. The primer will also be used to develop a site map for the Web site in late 2009; SAE documents will continue to be revised so that they will continue to be relevant as fuel cell vehicle development moves forward. Revisions reflect unique aspects of fuel cell vehicles and harmonize requirements with international standards. Future document revisions include *SAE J2578, J2799, J2579 and FTA or FMEA for H2 Refueling Process*. SAE will continue to compile necessary test data for an engineer to access the suitability of using a specific commodity plastic for containment of hydrogen; the intent is to collect this information and have it included in a central source thus facilitating reference by standards development organizations and other interested parties. A secondary objective is to generate a comprehensive testing list to facilitate the evaluation of newly developed materials. SAE International shall continue to provide technical expertise and administrative services/support to the USTAGs of ISO TC22 SC21, ISO TC197, International Electrotechnical Commission, and other groups and agencies as directed by DOE pertaining to the development of fuel cell vehicles, fueling stations, and other interface technologies.

Special Recognitions & Awards/Patents Issued

1. Kelvin Hecht was recipient for 2008 of the International Electrotechnical Commission’s annual award for outstanding service to TC105 fuel cell standards.

FY 2009 Publications/Presentations

1. All of Regulatory Logic LLC’s subcontractors presented a variety of presentations as described in their individual annual reports. Regulatory Logic LLC presented a poster at the Hydrogen Program and Vehicle Technologies Program Annual Merit Review and Peer Evaluation Meeting this past year, May 13–17, 2009.

IX.9 Hydrogen Optical Fiber Sensors

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Contract Number: DE-FG36-08GO88098

Project Start Date: June 1, 2008
Project End Date: May 31, 2010

Objectives

- Refine and optimize indicators and polymer materials for hydrogen detection in different optical guiding formats, including optrodes and waveguides as point sensors and optical fibers as distributed sensors.
- Optimize the sensor element fabrication techniques to develop a multi-channel sensor chip.
- Demonstrate the sensor's ability to achieve the required sensitivity with no oxygen or humidity dependence.
- Design and interface optical coupling techniques for waveguide and distributed optical fiber hydrogen sensors.
- Deliver a complete optoelectronic package for point and distributed hydrogen sensors.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Safety section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan (MYRDDP):

- **Delivery:** Barrier I. Hydrogen Leakage and Sensors (MYRDDP page 3.2-20: "Low cost hydrogen leak detector sensors are needed")
- **Storage:** Barrier H. Balance of Plant (BOP) Components (MYRDDP page 3.3-14: "Light-weight,

cost-effective... components are needed...These include... sensors")

- **Manufacturing:** Barrier F. Low Levels of Quality Control and Inflexible Processes (MYRDDP page 3.5-11: "Leak detectors... are needed for assembly of fuel cell power plants.")
- **Technology Validation:** Barrier C. Lack of Hydrogen Refueling Infrastructure Performance and Availability Data (MYRDDP page 3.6-8: "... the challenge of providing safe systems including low-cost, durable sensors [is an] early market penetration barrier")

Contribution to Achievement of DOE Safety, Codes & Standards Milestones

This project will contribute to achievement of the following DOE milestones from the Hydrogen Safety/ Leak Detection Technology section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- MYPP Milestone: Develop sensors meeting technical targets. (4Q, 2012)
- MYPP Milestone: Develop leak detection devices for pipeline systems. (4Q, 2015)

Accomplishments

This project was initiated on June 1st, 2008. Experimental work started by building on previous efforts in developing both the point sensor and distributed sensor formats. One of the major limitations that needed to be addressed was the activation step, during which the sensor films are heated to high temperatures (300-350°C). This heating step is needed to activate the catalyst precursor yielding a sensor matrix with a high degree of attenuation. In order to overcome this issue, we established collaboration with Raymat, Inc. to help in the development of heat tolerant, yet permeable, polymers for both applications: distributed optical fiber cladding, and high refractive index waveguide elements.

- Evaluated heat tolerant, low refractive index-matching polymers for fiber cladding applications. A hydrogen sensitive fiber cladding was fabricated and tested against various hydrogen concentrations down to 10% lower flammability limit (LFL). The cladding shelf-life aging was studied for ~9 months with good stability results.
- Evaluated heat tolerant, high refractive index polymers for waveguide applications. The hydrogen

sensitive waveguide approach had attenuation limitations, thus an attenuated total reflection (ATR) testing mode was used to achieve higher sensitivity through multiple optical paths. The cladding shelf-life aging was studied for ~6 months with satisfactory results.

- The optrode preparation scheme was optimized through the indicator solution infusion, reduction, and drying steps. The optrodes were tested against various hydrogen concentrations down to 10% LFL. Efforts in this project included optimization of the performance of previous optrodes in elevated humidity environments (>90% relative humidity). The reproducibility of the optrode fabrication, and the quality control of the resulting elements, will be targeted in the future work plan.
- Optical components were selected and the system design was outlined.

Introduction

IOS is leveraging its unique capabilities and expertise in optical sensors to develop reliable and sensitive hydrogen leak detectors with a wide dynamic range. The primary focus was on the development of sensor formats for two distinct embodiments: point sensors and distributed sensors. Point sensors are those that detect and measure a gas at a single location. Multiple point sensors are frequently used to simulate distributed sensor coverage. Truly distributed sensors can be realized by fabricating optical fibers whose light-confining cladding is a hydrogen sensitive polymer. Using optoelectronic methods developed at IOS, the distributed sensor will not only be able to sense hydrogen along its entire length, but will also be able to indicate, along the fiber length, the location at which the hydrogen has been released.

Point sensors are being explored in two major formats. The first is in the form of “optrodes,” where hydrogen indicator chemicals are deposited on a porous substrate. Optrode sensors can be completely passive, located at one end of an optical fiber, and probed by sending light through the optical fiber and observing the intensity of the reflected signal. This is especially attractive in situations where it is undesirable or difficult to introduce electrical devices. Optrodes can also be mounted directly between a light source and detector to achieve compact detection. The second type of point sensor will be in the form of an integrated optical waveguide. In this form, the sensor, optics, and electronics will all be located on a common chip, much as in semiconductor fabrication. In this latter example, the sensor chemistry could be incorporated either in a porous matrix or in a solid polymer, as long

as the chemistry is compatible with processes for chip fabrication. In both configurations, the hydrogen sensor element can be integrated with humidity, oxygen, and temperature sensor elements to eliminate the possible interference of these factors on hydrogen sensitivity.

Approach

IOS has studied three formats for hydrogen sensors: porous glass substrates (optrodes), evanescent-field polymer-clad silica optical fiber sensors (distributed sensors), and integrated-optic chip sensors.

A comparative evaluation of the various sensor matrices has revealed that, overall, the porous glass sensors (optrodes) performed the best. Thus, these were chosen as the hydrogen indicator matrix that will be used in the final product prototype. The sensor prototype design has been outlined and optoelectronic components have been acquired. The optrode response time is quite rapid (time to reach 90% of full-scale, $T_{90} \approx 10$ seconds); software routines will be developed to provide a warning of 10% LFL concentrations in one second by analyzing sensor dynamic response.

Results

Distributed Optical Fiber Approach

Polymers with refractive indices lower than borosilicate glass were investigated for application as a distributed optical fiber cladding ($n < 1.43$). In this project, IOS has developed and demonstrated the world's first fully distributed hydrogen transducer: an optical fiber that responds to hydrogen over its entire length. Although the fiber sensor development task is now complete, a long-term study of the hydrogen fiber cladding material stability is being carried out.

In order to develop a successful optical fiber cladding, and lower the optical attenuation in the evanescent field region, we investigated various indicator doping levels. The heat activation step that is required to reduce the catalyst also increases the optical attenuation because it causes a coloration of the indicator cladding layer. The fiber was exposed to a 4/3/2/1/0.4% hydrogen ladder using air as the carrier gas; the results shown in Figure 1 represent the sensitivity of one meter exposed sensor fiber over this dynamic range.

Integrated Sensor Chip (Polymer Waveguide Approach)

Polymers with refractive indices higher than silica were investigated for application as a waveguide array ($n > 1.48$). In order to function as an optical waveguide to contain and guide the transmission of light through

FIGURE 1. One Meter Hydrogen Sensor Fiber Response to Hydrogen Concentration “Ladder” in Dry Air

the structure, the refractive index of the guide must be higher than that of its surroundings. The high refractive index optical conductive polymer, IOS 146 ($n=1.460$), was evaluated for humidity interference, hydrogen sensitivity, and thickness dependence. A hydrogen colorimetric indicator was immobilized in IOS 146; the results showed promising sensor performance to LFL and 10% LFL levels of hydrogen in single-pass transmission mode (i.e., when the light signal measuring the optical absorbance change due to hydrogen exposure is passed through and perpendicular to the sensor film). We use this test mode for the initial screening and evaluation of all of our indicator chemistry formulations prior to incorporation into specific sensor formats. This particular combination of polymer and colorimetric indicator proved to be too high in absorbance (too dark) to be useful in waveguide mode (in which the light is guided longitudinally through a length of sensor material). While it is often desirable to pass the light through as much sensor material as possible in order to maximize exposure path length, in this case, since high optical attenuation prevents waveguide mode operation, we attempted a different route to light propagation in the sensor: an ATR mode. In true ATR, light is launched into the film through a prism at an angle such that a portion of the incident light traverses the film in multiple reflections until it is collected at the far end in the photodetector. The purpose of this method is to increase the exposed path length of the optical signal, thereby enhancing sensitivity beyond that which can be achieved in single-pass transmission mode. Unfortunately, even with two discrete reflections, the dark sensor film attenuated the optical signal below detection limits.

Using this technique, the light incidence angle θ was varied from 41° to 45° and the sample was challenged with hydrogen at the LFL at each setting. The incident angle 43° was used in sensitivity test measurements where the hydrogen sensor film was exposed to 4%, 0.5%, and 0.1% H_2 in air. Figure 2 represents the response of the sensor film in reflection mode when

FIGURE 2. Reflection Measurements with Exposures at 4, 0.5, 0.1% Hydrogen

the hydrogen gas was introduced after a 60 second conditioning period. Both sensor response time and signal magnitude were improved in reflection mode over the performance achieved in single-pass transmission mode.

Integrated Sensor Cassette (Porous Glass Approach)

The steps for processing porous glass sensor substrates into hydrogen-sensing optrodes were refined and documented. Process steps include cleaning the raw substrates, and then etching and impregnating the glass matrix with IOS hydrogen indicator. Optrodes prepared under these procedures showed enhanced response (over earlier efforts) to hydrogen at 4, 3, 2, 1, and 0.4% cycled with air. Figure 3 shows the response performance of four optrodes; three were prepared within a single batch, while the fourth optrode was prepared in a second batch to verify process control. The data shows comparable response to hydrogen in response would need to be accounted for by signal processing in a practical system. The upward “jump” of the baseline (0% H_2) signals for two of the optrodes, indicating increased transmission after the first exposure to hydrogen, is irreversible. This implies that optrodes may need to be preconditioned at the manufacturing facility before deployment. Optimization in the optrode fabrication process was continued using 10 mm optrodes, with the goal of achieving reproducibility with $<10\%$ signal strength deviation (permissible) from the mean value.

Optrode substrates were studied for their response to 4% H_2 at various humidity levels to evaluate their applicability in different environments. The substrates were preconditioned for one hour at the desired humidity prior to hydrogen gas introduction. At room

FIGURE 3. Response of Optimized Hydrogen Sensor Optrodes to Varying Hydrogen Concentrations in Dry Air

temperature, humidity levels were ramped up from 5% to 50% and 95% relative humidity. The uncoated optrodes appear suitable for use in environments ranging from “bone dry” to “tropical.” However, to forestall unanticipated problems with aging in aggressive environments, we will also investigate the performance of optrodes with single- and dual-layer humidity barriers composed of polymeric coatings (e.g., Cyclic Olefinic Polymer 10%CO₈007, and Soluble Perfluoro Polymer AF1600 6.0% in Fluorinert FC-770), and other hydrophobic materials

Optoelectronic Package

Sensor Hardware

We are designing a re-configurable stand-alone sensor module. The module schematic design is near completion. The unit will incorporate a microcontroller with digital signal processing capabilities and a built-in universal serial bus peripheral interface controller (USBPIC). Our research determined that the USBPIC 24 family by Microchip was most suitable, both for cost and architecture reasons.

The prototype will support four channels: signal, reference, temperature and humidity. The module’s interface will include both USB and RS232 serial communication. The design is illustrated in Figure 4.

Optical receivers with dynamic range exceeding 80 dBs have been developed at IOS; similar principles will be utilized in the hydrogen sensor optoelectronic module once the optrode designs are finalized, and optrode cassette light attenuation and response are fully characterized. The architecture includes light emitting diode (LED) drivers, sensor inputs, a user interface consisting of a keyboard and a liquid crystal display (LCD), and communications interfaces. Later

FIGURE 4. Illustration of the Hydrogen Sensor Prototype

in development, we will examine a controller-area network, which is utilized in the vehicle industry, and wireless expansion options (consisting of either SYNAPSE, ANT, or Zigbee).

Software

A dsPIC development board and C compiler were purchased and installed. Initial code building blocks were established for panel testing. Signal measurement and analysis goals previously acquired will be implemented using C code to take advantage of the microcontroller’s extensive capabilities.

Modules for keyboard input, LCD output, alarm algorithms, environmental and aging compensation, and data logging will be implemented after completing the basic routines for controlling the hardware.

Conclusions and Future Directions

- Continue studying the optrode hydrogen sensor fabrication and process control.
- Study different humidity barriers to optimize the optrode’s response in the presence of elevated humidity levels.
- Evaluate the lifetime of the chosen optrode hydrogen sensors.
- Design the optoelectronic interface into a compact sensor chip that will include the selected LED and photodiodes in a modular sensor package.
- Design and validate the data processing and algorithms.
- Explore commercial possibilities for the different hydrogen sensor embodiments.

FY 2009 Publications/Presentations

1. 2009 Annual Merit Review Proceedings, poster presented May 20, 2009.

X. EDUCATION

X.0 Education Sub-Program Overview

Introduction

The Education Sub-Program seeks to support and facilitate hydrogen and fuel cell demonstration, deployment, and market transformation by providing technically-accurate and objective information to key target audiences that can help transform the market (see Table 1).

TABLE 1. Key Target Audiences for the Education Sub-Program

Target Audience	Rationale
Code Officials	Code officials must be familiar with hydrogen to facilitate the permitting process and local project approval.
First Responders	Fire fighters, as well as law enforcement and emergency medical personnel, must know how to handle potential incidents; their understanding can also facilitate local project approval.
Local Communities/ General Public	Local communities will be more likely to welcome hydrogen and fuel cell projects if they are familiar with hydrogen.
Potential End-Users	Potential early adopters need information about commercially available hydrogen and fuel cell products and the opportunities for incorporating the technology into their operation.
State and Local Government Representatives	A broad understanding of hydrogen supports decision-making on current opportunities for near-term deployment and lays the foundation for long-term change.
Teachers and Students	Teachers are looking for technically accurate information and usable classroom activities.
University Faculty and Students	Graduates are needed for research in government, industry, and academia.

The Education Sub-Program includes the development and dissemination of information resources as well as training. It considers a balanced message to help target audiences become familiar with hydrogen and how it fits in the portfolio of energy choices, develop an accurate understanding of hydrogen safety, recognize opportunities for deployment in near-term markets, and understand their part in facilitating use of hydrogen and fuel cell technologies.

Goal

Educate key audiences about hydrogen fuel cell technologies to facilitate near-term demonstration and long-term commercialization and market acceptance.

Objectives

Education objectives are based on national, statistically-valid knowledge surveys. An initial survey conducted in 2004 provides a baseline from which the sub-program can measure changes in knowledge over time. The baseline for each target population is defined as that population's average score on the survey's technical knowledge questions. Objectives are:

- By 2009, increase knowledge of hydrogen and fuel cell technologies among key target populations (compared to a 2004 baseline):
 - Increase understanding of hydrogen and fuel cell technologies among state and local governments and students (ages 12-17) by 10%.
 - Increase understanding of hydrogen and fuel cell technologies among the public and potential end-users by 15%.
- By 2012, increase knowledge of hydrogen and fuel cell technologies among key target populations (compared to a 2004 baseline):
 - Increase understanding of hydrogen and fuel cell technologies among state and local governments and students (ages 12-17) by 20%.

- Increase understanding of hydrogen and fuel cell technologies among the public and potential end-users by 30%.

Fiscal Year 2009 Status

The Education Sub-Program works in collaboration with the Safety, Codes, and Standards Sub-Program to provide objective and technically-accurate information to the safety community, including fire, law enforcement, and emergency medical personnel. In FY 2009, the subprogram completed and conducted several sessions of a new hands-on “prop course” for fire fighters. This advanced-level one-day course builds on an introductory course launched in 2007, but provides more detail and includes a hands-on training component and training scenarios to demonstrate the safe approach to a fuel cell vehicle, extinguishment of a compartment fire, extrication techniques, and hydrogen venting during a compartment fire. The Web-based “Introduction to Hydrogen Safety for First Responders” was updated to include audio narration, an extended video, a revised quiz, and a certificate of completion. The subprograms also launched an introductory course designed specifically for code and permitting officials. Like the introductory course for first responders, “Introduction to Hydrogen Safety for Code Officials” is a 5-module, Web-based course that provides a general overview of hydrogen and its properties and applications, but also includes additional information on the technology and equipment tailored to the needs of code and permitting officials.

In FY 2009 a new early market outreach project provided potential end users with real-world experience through month-long deployments of two hydrogen fuel cell-powered lift trucks at high-profile geographically diverse locations. Complementary workshops targeted toward facilities management, operators, maintenance personnel, health and safety groups, first responders, authorities having jurisdiction, technical and community colleges, and the general public used these deployments to demonstrate the economic and environmental benefits of fuel cells.

The Education Sub-Program expanded its efforts to reach out to and partner with state and local governments through seven new state and government outreach projects. These outreach efforts focused on states with an active hydrogen and fuel cell presence to develop case studies, best practices, and technical assistance resources to help decision-makers identify and assess opportunities for future deployment. In collaboration with partners, the sub-program continued to host the Bi-monthly Informational Conference Call Series for State and Regional Hydrogen and Fuel Cell Initiatives, bringing together state groups to network and share lessons learned.

“H2 Educate!,” a set of lesson plans and activities for middle school teachers and students, continued to be disseminated through one-day teacher training workshops across the country. The companion effort for high schools, “HyTEC,” completed a national field test of a six-unit science curriculum on hydrogen and fuel cells. In FY 2009, the Education Sub-Program launched five new projects with universities, targeting a broad student audience with the development of general courses as well as specialized science and engineering programs through minor and concentration programs, courses, curriculum modules, internships, labs, lab kits, and textbook chapters.

In FY 2009, the Education Sub-Program moved to the Vehicle Technologies Program to build on synergy with related efforts for other alternative fuels and advanced transportation technologies. As part of this effort, Education activities expanded to include support for the Automotive X Prize and the contest’s education component, “Fuel our Future Now”, a Web site targeted toward K-12 students.

FY 2009 Accomplishments

- Launched advanced-level prop-based course for first responders in coordination with the Safety, Codes and Standards Sub-Program with input from a steering committee comprising representatives from auto companies, energy companies, and the fire safety community. This in-depth 8-hour course uses a one-of-a-kind hydrogen burn prop that simulates a fuel cell vehicle. Building on the “Introduction to Hydrogen Safety for First Responders,” the course has been developed to help first responders gain hands-on experience with personal protective equipment, monitoring and detection equipment, and the basic control, containment, and confinement

operations associated with fuel cell vehicles and stationary applications. After two pilot courses in December and March for technical and industry representatives, DOE has trained 36 first responders from 10 states with two trainings in June and August.

- Upgraded “Introduction to Hydrogen Safety for First Responders” Web-based course, in coordination with the Safety, Codes and Standards Sub-Program. Updates include the addition of an audio narration, an extended video on *The Characteristics of Hydrogen*, a revised quiz, and the addition of a certificate of completion. Since its launch in January 2007, an average of 300-500 users have accessed the course each month; user groups include the fire prevention/protection community, law enforcement, industry, universities, military, non-profits, and national and international users.
- Outreach efforts continued for both first responder courses with the dissemination of hydrogen safety literature and course CDs, promotion of the prop course, and demonstration of the small hydrogen flame prop at emergency responder conferences including Fire Department Instructor’s Conference and Fire Rescue International.
- Launched “Introduction to Hydrogen Safety for Code Officials” in coordination with the Safety, Codes and Standards Sub-Program. This e-learning package builds on modules in the introductory first responders’ course and includes additional information on technology and equipment tailored to the needs of code and permitting officials. Modules focused on fueling stations and stationary facilities present technical information essential to permitting hydrogen and fuel cell facilities. Outreach activities identified and connected with authorities having jurisdiction through Web sites, e-mails, newsletters and other publications. Course material was also distributed at five permitting workshops around the country.
- Launched a new early market outreach project to educate facilities management, operators, maintenance personnel, health and safety groups, first responders, authorities having jurisdiction, technical and community colleges, and the general public on the benefits of fuel cell forklifts through nine educational seminars targeted to lift truck users (90 total attendees) and two high-profile conferences. In parallel, month-long deployments of two hydrogen fuel cell-powered lift trucks at high-profile geographically diverse locations provided real-world experience and showcased the economic and environmental benefits of fuel cells. So far, the project has completed one successful deployment at Stanley Tool with an additional five sites planned at Lowe’s, Michelin Tire, Bausch & Lomb, Electrolux, and UTi.
- Launched new state and government outreach projects in states with an active hydrogen and fuel cell presence including Connecticut, Texas, Ohio, South Carolina, Virginia and two national groups. These seven projects have conducted 11 workshops and Webinars across the country in addition to producing Web sites, video, and print articles to educate state and local government officials. During the first year, these groups have developed technology basics curricula, case studies, best practices, and technical assistance resources to help decision-makers identify and assess opportunities for future deployment.
- Continued state and local government outreach with the Bi-monthly Informational Conference Call Series for State and Regional Hydrogen and Fuel Cell Initiatives. Featured topics included hydrogen and fuel cell tax incentives and state and national strategic plans. In addition, to the bi-monthly calls, an in-person meeting at the National Hydrogen Conference allowed participants and experts to meet in small groups to network and discuss topics relevant to state and local hydrogen and fuel cell initiatives.
- Launched new university education projects at California State University, Los Angeles, Humboldt State/University of California, Berkeley, Michigan Tech, the University of Central Florida, and the University of North Dakota. These five projects have developed a total of 22 courses and curriculum modules for general science and engineering programs and specialized hydrogen and fuel cell concentrations. Universities are building labs and sponsoring teaching assistantships and internships to provide hand-on experience with the technology. Lab kits and textbook modules will be integrated into existing science and engineering teaching materials to introduce hydrogen and fuel cell technology to university students across the country. These education materials are targeting a broad student audience in general courses and specialized science and engineering programs

- Continued to disseminate the middle school teacher and student “H2 Educate!” curriculum through one-day teacher training workshops across the country. Since its inception, the program has reached over 7,000 middle school teachers through workshops and conference sessions. Teacher and student guides are available via the DOE Hydrogen Program Web site (www.hydrogen.energy.gov) and www.need.org.
- The Hydrogen Technology and Energy Curriculum Project (HyTEC) for high schools completed a nation-wide field test by 13 science teachers of a six-unit curriculum. More than 600 high school students and 100 high school teachers have been introduced to hydrogen and fuel cell course materials.
- Continued audience-targeted Hydrogen Program exhibit outreach to early end-user conferences (e.g. ProMat 2009, International Warehouse Logistics Association 118th Annual Convention) and safety community conferences (e.g. Fire Rescue International) in addition to hydrogen and fuel cell conferences. A new portable fuel cell-powered booth lights to showcase the technology.
- Completed the 2008/2009 Hydrogen Knowledge and Opinions survey and analysis with plans to publish a report in the fall of 2009. This effort follows the baseline survey conducted in 2004 and will also include a separate survey of code officials – an audience that had been previously incorporated into the state and local officials survey population but have been prioritized as a key target audience essential to the early adoption of fuel cells.
- Partnered with the Clean Cities Program, the Automotive X Prize, and Discovery Education to launch “Fuel our Future Now” an educational Web site on advanced transportation technologies. The Web site premiered at the Washington D.C. Auto Show in February 2009 and features curriculum modules for students K-12.

Budget

The FY 2009 Education Sub-Program budget was \$4.2 million; an increase from the previous year and the highest it has been since FY 2004.

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X.1 Hydrogen Safety: First Responder Education

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Subcontractors:

- *Volpentest Hazardous Materials Management and Emergency Response (HAMMER) Training and Education Center, Richland, WA
- **California Fuel Cell Partnership (CaFCP), Sacramento, CA

Project Start Date: October 1, 2004

Project End Date: Project continuation and direction determined annually by DOE

Objectives

- Support the successful implementation of hydrogen and fuel cell demonstration projects and market transformation by providing technically accurate and objective information about hydrogen to first responders.
- Launch an in-depth, one-day course for first responders utilizing DOE's mobile hydrogen fuel cell vehicle (FCV) prop.
- Continue to update the awareness-level course first launched in Fiscal Year 2007.
- Disseminate first responder hydrogen safety educational materials at appropriate conferences.

Technical Barriers

This project addresses the following technical barriers from the Education section of the Hydrogen, Fuel Cells and Infrastructure Technologies (HFCIT) Program Multi-Year Research, Development and Demonstration Plan:

- (A) Lack of Readily Available, Objective, and Technically Accurate Information
- (C) Disconnect Between Hydrogen Information and Dissemination Networks

- (D) Lack of Educated Trainers and Training Opportunities

Contribution to Achievement of DOE Education Milestones

This project will contribute to achievement of the following DOE milestones from the Education section of the HFCIT Program Multi-Year Research, Development and Demonstration Plan:

- **Milestone 4:** Update "Awareness-Level" information package for first responders (4Q, 2009)
- **Milestone 6:** Update "prop-course" for first responders. (4Q, 2011)
- **Milestone 7:** Update "Awareness-Level" information package for first responders. (4Q, 2012)
- **Milestone 9:** Update "prop-course" for first responders. (4Q, 2014)
- **Milestone 10:** Update "Awareness-Level" information package for first responders. (4Q, 2015)

In addition, the following milestones were met in previous years:

- **Milestone 1:** Develop "Awareness-Level" information package for first responders (4Q, 2006)
- **Milestone 3:** Develop "prop-course" using hands-on training devices for first responders (4Q, 2008)

Accomplishments

- **Improved the Awareness-Level Course:** Developed a new video *The Characteristics of Hydrogen* that compares the properties and characteristics of hydrogen with those of conventional fuels that are familiar to first responders. Created narrated transcript so viewers can listen to course content instead of reading it. Revised quiz questions and answers, and added a certificate of completion for users who take the quiz. Launched new Web site on the PNNL server. Distributed compact disk (CD) version of course to users who request copies via the Web site.
- **Conducted Effective Outreach Activities:** Distributed CDs and print versions of the awareness-level course, as well as posters and *Firehouse* article reprints about the course, through the DOE Energy Efficiency and Renewable Energy (EERE) Information Center. Hosted booths at key first responder conferences.
- **Developed Prop-Based Course:** Developed course modules in the form of PowerPoint slides and notes pages. Developed a more in-depth study guide to

accompany the slides. Packaged the slides, notes pages, study guide, Web-based awareness-level course CD, and *The Characteristics of Hydrogen* digital video disk (DVD) into a course binder that is distributed to all students. Curriculum was completed and reviewed by DOE. First pilot course held on December 2, 2008 for technical reviewers from several national laboratories. Second pilot course held for industry representatives on March 10, 2009. Curriculum was revised slightly after each pilot course. First “real” courses held on June 16, 2009 and August 18, 2009 for first responders from across the country.

Introduction

Safety in all aspects of a future hydrogen infrastructure is a top priority, and safety concerns influence all DOE hydrogen projects. Despite the most concerted effort, however, no energy system can be made 100% risk-free. Therefore, for any fuel, a suitably trained emergency response force is an essential component of a viable infrastructure. HFCIT has identified training of emergency response personnel as a high priority, not only because these personnel need to understand how to deal with a hydrogen-related emergency situation, but also because firefighters and other emergency workers are influential in their communities and can be a positive force in the introduction of hydrogen and fuel cells into local markets.

This project is employing the Occupational Safety and Health Administration and National Fire Protection Association frameworks for hazardous materials emergency response training to develop a tiered hydrogen safety education program for emergency responders. The overall first-responder education program will be developed over a number of years. The effort started with development and distribution of the awareness-level Web-based course developed in FY 2006-2007. A more advanced course and materials to facilitate education were developed in FY 2008 and FY 2009, complementing the development of a FCV prop (developed under PNNL's companion Hydrogen Safety Project). In addition, PNNL has implemented outreach efforts to key stakeholder groups in order to facilitate delivering the training to a broad audience.

Approach

PNNL works with experts in hydrogen safety and first responder training (e.g., the PNNL Hydrogen Safety Panel, other national laboratories, HAMMER, CaFCP), to develop hydrogen safety course materials. Draft materials are prepared and undergo considerable review and revision before being released. PNNL (with

subcontractor support, as needed) works with DOE to develop plans for making stakeholder groups aware of training opportunities, and to provide “live” training when appropriate.

Specific tasks in FY 2009 included the following:

- **Update the Web-based first responder awareness-level hydrogen safety course.** The *Introduction to Hydrogen Safety for First Responders* course is designed for first responders who may be called to or witness an accidental release of compressed or liquid hydrogen and must initiate an emergency response by notifying other responding authorities, but who would not be expected to take further action. The target audiences in this group include firefighters, police, and emergency medical technicians. The introductory online course consists of a combination of presentation slides with videos and animations for illustrating key points, such as relevant aspects of hydrogen behavior, along with narration to enhance the learning experience. The Web-based format lends itself to use with a wide variety of media; in addition to the course being made available over the Internet, it is also being distributed on CD and PDF (printed hard copy). In FY 2008 and FY 2009, PNNL and HAMMER reformatted the training, added an oral transcript and a new video on hydrogen properties and behavior, included new material on stationary sources and codes, revised quiz questions and answers, added a certificate of completion, and made other minor modifications. The course was finalized in February 2009.
- **Awareness-level outreach.** PNNL and HAMMER supported efforts to distribute information about the *Introduction to Hydrogen Safety for First Responders* course to its target audiences. HAMMER staff attending several conferences (with a booth to demonstrate the course). CDs, flyers and posters containing course material were also distributed through the EERE Information Center.
- **Complete development of prop-based course on hydrogen safety.** While all first responders should understand the fundamentals of hydrogen safety provided in the introductory course, most emergency personnel in regions with hydrogen demonstrations or emerging hydrogen infrastructure should aspire to a more in-depth level of understanding. An 8-hour course that utilizes a one-of-a-kind hydrogen burn prop that simulates a FCV has been developed to help first responders gain hands-on experience with personal protective equipment, monitoring and detection equipment, and the basic control, containment, and confinement operations associated with hydrogen FCVs and stationary applications. Pilot courses were held first to get feedback on improving the

curriculum, and then actual first responder classes were held in the summer of 2009.

Results

Web-based course: The introductory course was revised during FY 2008, although the basic content remained the same as the earlier version. For each topic, a separate module provides basic information and sometimes videos or animations to further explain particular points.

Since the initial version of the online course was launched in January 2007, there have been more than 12,000 unique visitors to the Web site. The site is still averaging 300-500 unique visitors each month from almost every state and many foreign countries. Typical viewers include the fire prevention/protection community, firefighters, fire department education coordinators, fire marshals, fire plan examiners/inspectors, code officials, law enforcement officials, and representatives from industry, universities, the military, and non-profit organizations. Feedback on the course has been quite positive.

Outreach: To distribute information and raise awareness about hydrogen safety and about the DOE-sponsored courses, HAMMER staff participated in two major first-responder conferences in FY 2009 to raise awareness about hydrogen safety and the DOE-sponsored courses:

- Fire Department Instructor's Conference, April 2009, Indianapolis
- Fire Rescue International, August 2009, Dallas

Booths were set up to display and disseminate posters, announcements of course offerings, hydrogen safety literature, and awareness-level course CDs. Also, HAMMER conducted live flame prop demonstrations at the Fire Department Instructor's Conference.

Prop course: Based on guidance from subject matter experts in industry and the national labs, as well as local

first responders who attended the pilot courses, the prop course was developed in several modules:

- Introduction and Course Overview
- Hydrogen and Fuel Cell Basics
- Hydrogen Vehicles
- Stationary Facilities
- Emergency Response
- Classroom Exercise: Incident Scenarios
- Quiz
- Hands-On Exercise with FCV Prop

The course uses existing, vetted materials as much as possible. Information on technical issues (e.g., the components of a FCV) is integrated with instruction on the appropriate safety-related emergency responses. The focus of the curriculum is on teaching first responders what is the same and what is different about hydrogen and FCVs as compared to conventional fuels and vehicles. We distribute a course evaluation form at the beginning of each class to request feedback from participants that will help us improve the course content and delivery. Based on feedback from both pilots and the first "real" class sessions, we conclude that first responders are comfortable with hydrogen as an energy carrier. In fact, many of them stated that they feel it is safer than gasoline. PNNL is pursuing official endorsement of this curriculum through the National Fire Academy's State Fire Training Course Endorsement Program.

The FCV prop (shown in Figure 1) demonstrates potential conditions that could be encountered during the control and suppression of a FCV fire. The prop has been integrated into the "Hydrogen Emergency Response: Training for First Responders" course developed by PNNL and HAMMER for DOE. The figure shows a team of firefighters responding to a multi-vehicle accident involving a hydrogen FCV and two conventional vehicles.

FIGURE 1. FCV Prop Training Exercise

Conclusions and Future Directions

The introductory Web-based course has been quite successful, based on the usage recorded and feedback received. The course is fulfilling a need expressed by the first responder community to receive more information about hydrogen and fuel cells so they will be prepared in the rare event of a hydrogen-related emergency. The in-depth prop-based course builds on that success and is expected to be very useful in giving first responders a hands-on experience with simulated FCV incidents.

In future years, PNNL will continue to update the awareness-level and prop-based courses. PNNL will work with DOE to give the prop-based course at HAMMER and other locations in FY 2010. PNNL will also work with DOE to determine what, if any, additional types of educational courses are warranted, and to develop and implement plans to provide education to specific groups.

FY 2009 Publications/Presentations

1. Placet, M. *Hydrogen Safety: First Responder Education*, PNNL-SA-65774, 2009 U.S. DOE Hydrogen Program and Vehicle Technologies Program Review and Peer Evaluation, Arlington, VA, May 21, 2009.

X.2 Hydrogen Education for Code Officials

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Subcontractors:

- Battelle, Columbus, OH
- Ecommerce Systems, Inc., Greenwood Village, CO
- Adrenaline, Boulder, CO

Project Start Date: October 1, 2007

Project End Date: October 30, 2009

Objectives

Develop an introductory information (e-learning) package for code officials that specifically addresses safety, codes, and standards for hydrogen technologies and facilitates demonstration and deployment projects.

Technical Barriers

This project addresses the following technical barriers from the Education section (3.9) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) **Lack of Readily Available, Objective, and Technically Accurate Information**
Although a significant body of technical information exists, there is little readily available information about hydrogen and fuel cells for individuals outside of the research and development community, and many educational resources and training opportunities require participants to pay a fee. Moreover, explaining hydrogen and fuel cells to a non-technical audience – clearly and succinctly, while still retaining technical accuracy – is challenging.
- (C) **Disconnect Between Hydrogen Information and Dissemination Networks**
Educational materials and resources must reach their intended audiences to be effective, and institutional barriers can complicate or inhibit target audience access to information. Many target

audiences have established training mechanisms and legacy networks through which they are accustomed to receiving information. Tapping into these traditional training and education mechanisms is often the most efficient way in which to ensure access to the target audience, but it is often difficult to do.

(D) **Lack of Educated Trainers and Training Opportunities**

In-person training through workshops or seminars is one of the most effective information delivery mechanisms – there is less distraction for students and an opportunity for interaction between and among all participants. Availability of suitable trainers is low, however, and can be resource-intensive at a level that is cost prohibitive for most education programs.

Contribution to Achievement of DOE Education Milestones

This project will contribute to achieving the following DOE milestones from the Education section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- **Milestone 2:** Develop introductory package for code officials. (2Q, 2008)
- **Milestone 5:** Update introductory information package for code officials. (4Q, 2010)
- **Milestone 8:** Update introductory information package for code officials. (4Q, 2013)

Accomplishments

- Module 1–Hydrogen and Fuel Cell Technology Basics
 - Includes basic hydrogen and fuel cell properties, production, storage, and applications.
- Module 2–Hydrogen and Fuel Cell Applications
 - Provides the learner with a detailed look at hydrogen and fuel cell applications and how they work.
- Module 3–Permitting Hydrogen Fueling Stations
 - Provides examples of station designs and the codes and standards that could apply to hydrogen fueling stations as well as an interactive station design.
- Module 4–Permitting Fuel Cell Facilities
 - Educates the learner on aspects of permitting a hydrogen stationary facility, provides examples

of facility designs and the codes and standards that could apply as well as an interactive telecommunication facility graphic that provides the separation distances and codes and standards for the facility.

Introduction

The National Renewable Energy Laboratory (NREL) is developing an e-learning package for code officials. The courses in this package introduce code officials to hydrogen and fuel cells, hydrogen and fuel cell applications, and the safety, codes, and standards currently used for hydrogen technologies. This information will help facilitate demonstration and deployment projects across the nation.

The challenge of this project is the decentralized enforcement of codes or adopted standards. About 44,000 different jurisdictions in the United States use existing codes and standards by either incorporating appropriate sections, or by referring to those sections. States and municipalities may also impose more stringent or additional requirements. Incorporated content of codes and standards is enforceable by law. These modules will provide a uniform starting point for code officials and facilitate the permitting process.

Approach

To develop the code official learning package, we evaluated e-learning tools, methods, and software available to determine the most suitable approach for presenting the information. A detailed outline for each course was developed. Codes and standards as well as hydrogen experts then reviewed the content to ensure accuracy.

The e-learning resources are designed to maximize usability and engage the learner. Studies have shown that interaction between the learner and the software increases the information that learners remember upon completion. An example of this is the test-question method shown in Figure 1. At the end of each lesson, the learners are asked a series of questions about the content that was presented and they receive instant feedback about their answers.

Results

Module 1 is an introduction to hydrogen and fuel cells, which includes hydrogen properties, production and storage methods, and applications. Figure 2 displays the course content and navigation pages that the learner can access at any time by clicking on the course map tab

FIGURE 1. Screen Shot Showing Example of Test-Question Method

FIGURE 2. Screen Shots Displaying Course Content and Navigation Pages

at the top. This enables the learner to take the lessons in the course in any order or study just one or two lessons depending on their level of knowledge.

Module 2 provides a detailed look at fuel cells and their applications. It describes the common types of fuel cells, how each type works, and the applications for which they are best suited.

Module 3 provides the applicable codes and standards for permitting hydrogen fueling stations and has a fueling station design at the end that can be used as an example and includes the separation distances, and codes and standards that apply to that station design.

Module 4 addresses stationary hydrogen fuel cell facilities and provides examples of the codes and standards used to permit the construction and operation of these facilities. An interactive graphic is included that shows the separation distances and the codes and standards that apply (Figure 3).

Modules 3 and 4 are linked to a database that provides updated codes and standards as they become available.

The course is complete and available online at http://www.hydrogen.energy.gov/code_official_training.html. The content was put into a design template similar to the one used in the first responders online training developed by Pacific Northwest National Laboratory, meets 508 accessibility requirements, and contains an audio option. There is a library within the course that contains publications and other related information.

Conclusions and Future Directions

Future work will include the following:

- Content and usability will be reviewed by the hydrogen and code official community.
- Outreach activities, online resources, and publications will be used to distribute the information resources to the code official community.
- A Web page has been created to house and provide easy access to the Introduction to Hydrogen for Code Officials, along with the other online resources such as the First Responders Training.
- Interactive graphics will be updated when new separation distances become available.

FY 2009 Publications/Presentations

1. Hydrogen Conversion Factors and Facts Card
<http://www.hydrogen.energy.gov/permitting/pdfs/43061.pdf>
 - This conversion card contains basic facts about hydrogen, resource references, a fuel characteristics comparison chart, and conversion factors for common hydrogen measurements.
2. NREL Renewable Energy Permitting Workshops
 - February 11 & 12, Broomfield, CO
 - March 25, Los Angeles, CA
 - April 3, Columbia, SC
 - April 5, Seattle, WA

FIGURE 3. An example of a telecom backup power application (as pictured here) is provided in Module 4: Permitting Fuel Cell Facilities. It shows the learner applicable codes and standards as well as the separation distances.

X.3 Hydrogen and Fuel Cell Education at California State University, Los Angeles

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Contract Number: DE-FG36-08GO18106

Project Start Date: October 15, 2009
Project End Date: July 31, 2009

Objectives

California State University, Los Angeles, has partnered with the Department of Energy in addressing the workforce preparation and public education needs of the fuel cell industry and the U.S. economy through a comprehensive set of curriculum development and training activities:

- Developing and offering several courses in fuel cell technologies, hydrogen and alternative fuels production, alternative and renewable energy technologies as means of zero emissions hydrogen economy, and sustainable environment.
- Establishing a zero emissions proton exchange membrane fuel cell and hydrogen laboratory supporting curriculum and graduate students' teaching and research experiences.
- Providing engaging capstone projects for multi-disciplinary teams of senior undergraduate students.
- Fostering partnerships with automotive original equipment manufacturers (OEMs) and energy providers.

Technical Barriers

This project addresses the following technical barriers from the Education section (3.9.5) of the Hydrogen, Fuel Cells and Infrastructure Technologies

Program Multi-Year Research, Development and Demonstration Plan:

- (A) Lack of Readily Available, Objective, and Technically Accurate Information
- (B) Mixed Messages
- (D) Lack of Educated Trainers and Training Opportunities

Contribution to Achievement of DOE Education Milestones

This project will contribute to achievement of the following DOE milestones from the Education section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- **Milestone 11:** Develop set of introductory materials suitable for a non-technical audience. (4Q, 2006)
- **Milestone 21:** Launch new university hydrogen education program. (4Q, 2009)
- **Milestone 27:** Launch high school teacher professional development. (4Q, 2008 through 3Q, 2011)

Accomplishments

- In the 2008-2009 academic year, we developed course modules or completely new offerings in four courses: ME 454-Renewable Energy and Sustainability (enrollment 26); ME 554-Fuel Cell Systems (graduate course; enrollment 16); TECH 478-Fuel Cell Applications (enrollment 10 technology, 11 mechanical and 1 electrical engineering); TECH 250-The Impact of Technology on the Individual and Society. **M:21.**
- TECH 250-The Impact of Technology on the Individual and Society course is a general education required course, which contains one week module on fuel cells and the hydrogen economy. It is open to all majors in the university and is selected to deliver our message to the university-wide student body. Enrollment was as following: Fall 2008 – 31, 33, 30, 32 (4 sections were offered), Winter 2009 – 35, Spring 2009 – 25. **M:21.**
- Six faculty who are usually assigned to teaching TECH 250 were trained on the topic and provided teaching materials on fuel cells and the hydrogen station to be built on campus. See published materials section. **M:21.**

- Work has begun on the Zero Emissions Fuel Cell and Hydrogen Laboratory. Major equipment has been acquired: Heliocentris -- Dr. Fuel Cell, Nexa Training System Complete, Nexa Integration Kit; and Proton-Hogen GC600 Electrolyzer. Two graduate students were selected for educational and research projects in the laboratory. **M:21.**
- The College of Engineering, Computer Science and Technology (ECST) assembled a multidisciplinary senior design team which installed 21 solar panels (1.8 kW total power) donated by Southern California Edison and valued at \$5,000. The team consisted of four electrical engineering (EE) and one technology (TECH) student. The work will be continued to complete wiring and connection to the Zero Emissions Lab. CSULA published an article describing the project [1].
- ECST assembled a multidisciplinary senior design team to design and build a Hydrogen Safety demonstrator. The team consisted of two mechanical engineering (ME) and two EE students. The enabled experiments produced spectacular performance. For safety, the explosions are activated with a wireless remote. **M:21.**
- There has been an appreciable number of public outreach and educational activities through which fuel cell and hydrogen technologies and the new curriculum at CSULA were promoted. **M:11.**
- CSULA has continued to build its relationship with OEMs and the industry through its Hydrogen Station efforts, hosting the National Renewable Energy Laboratory's hydrogen station permitting workshops and other industry contacts.
- The technology student, who participated on the solar installation, completed courses in Advanced Engine Design, Hybrid and Electric Vehicles, and Fuel Cell Applications. He was hired as the automotive instructor at a local high school. **M:27.**

Introduction

Our interest in developing hydrogen and fuel cell education stems from the recognition of the urgent need for workforce development and public education in the entire spectrum of alternative and renewable energy technologies (ARET). ECST is taking steps to graduate more students fluent in ARET as well as to raise campus and state-wide awareness of green technologies. This includes our bid for a hydrogen fueling station on campus. The comprehensive nature of the university, its strategic location in the hydrogen and fuel cell abundant industrial region and a historically minority-serving charter make it an ideal candidate to carry out the tasks listed in the objectives.

Approach

Design of a comprehensive engineering and technology curriculum addressing fuel cells and hydrogen technologies is the foundation for our contribution toward green workforce training. This is accomplished through a mix of new courses or special modules in existing courses to introduce the concepts of fuel cell technologies, hydrogen and alternative fuels, alternative and renewable energy technologies as means of zero emissions hydrogen economy, and sustainable environment. Concurrently, ECST established a Zero Emissions Fuel Cell and Hydrogen Laboratory to support curriculum and graduate students' teaching and research experiences. Further, enrichment of student experiences is accomplished through projects and fostering partnerships with automotive OEMs and energy providers.

Community education and public outreach goals are met through a series of on campus and off-campus public events and demonstrations.

Results

Four courses either with integrated modules or fully dedicated were introduced into the interdisciplinary curriculum at ECST: ME 454-Renewable Energy and Sustainability, ME 554-Fuel Cell Systems, TECH 478-Fuel Cell Applications, TECH 250-The Impact of Technology on the Individual and Society. Significant developments were introduced in TECH 478. The Honda Clarity FCX team gave a lecture and a demonstration on Honda fuel cell vehicles, see Figure 1. As part of the final exam, students attended the 2009 American Society of Mechanical Engineers (ASME) Fuel Cell conference which was available locally. ASME sponsored student registration. At other occasions, General Motors fuel cell vehicle center in Burbank, CA,

FIGURE 1. CSULA students are studying Honda Clarity FCX fuel cell vehicle during Honda's visit.

as well as the Southern California Edison Electrical Vehicle Center in Pomona, CA, hosted CSULA students for tours. Attending the ASME conference and OEM participation greatly contributed to our objective of fostering partnerships with the industry.

Work has begun on establishing the Zero Emissions Fuel Cell and Hydrogen Laboratory. The laboratory is designed to provide hands-on activities supporting fuel cell courses offered in the program. Major equipment has been acquired: Heliocentris -- Dr. Fuel Cell, Nexa Training System Complete, Nexa Integration Kit; and Proton-Hogen GC600 Electrolyzer. The solar installation on the roof will provide the renewable generation of power for hydrogen electrolysis. A multidisciplinary senior design team designed and built a custom hydrogen safety demonstrator that allows to experiment with the comparative explosivity limits of hydrogen and other explosive gases, see Figure 2.

CSULA has actively pursued public outreach and educational activities through which the DOE-sponsored Fuel Cell and Hydrogen curriculum at CSULA is promoted. During the summer of 2008, a team of six summer undergraduate researchers representing four different states built a 25-cm² fuel cell test stand, see Figure 3. The test stand was taken to the Hydrogen Road Tour Day at the California Science Center in Los Angeles in August 2008. It was displayed at the Santa Monica Alternative Car Show in September 2008. During the fall of 2008, ECST hosted two open house events for middle and high-school students, about two hundred of whom toured the Zero-Emissions Fuel Cell laboratory. In February, the stand was a part of the Southern California Edison Black History Month event. On April 18, 2009, CSULA participated in the first annual "Green Valley Expo" organized by Lookin' Green Magazine, Pasadena, CA. The magazine also published our material explaining operation of a fuel cell

FIGURE 2. Hydrogen Safety Experiment Built by a Senior Design Team

FIGURE 3. Fuel cell test stand and a CSULA team of two faculty and a student representing innovative curriculum during Hydrogen Road Tour Day.

[2] online and in the hardbound copy. The magazine also placed an online article describing the CSULA Hydrogen and Fuel Cell program [3].

CSULA has partnered with East Los Angeles College to provide summer workshops to 15 college students. At the end of the program, a LEGO Mindstorm robot powered by a Horizon 20 W fuel cell was built. ECST is also executing its Research Experience for Undergraduates National Science Foundation program through which four students are working on various projects in the Zero Emissions Fuel Cell and Hydrogen Laboratory.

The principal investigator (PI) attended the 2009 Annual Merit Review in Washington DC, 2009, Hydrogen + Fuel Cells conference in Vancouver, Canada, and, 2009 ASME Fuel Cell conference, Newport Beach, CA. One research student and the PI attended the Short Fuel Cell Course at Los Alamos National Laboratory in August 2009.

Conclusions and Future Directions

CSULA has methodically pursued its objectives in executing the grant. The team has offered a comprehensive suite of courses addressing fuel cell and hydrogen technologies. The Zero Emissions Fuel Cell and Hydrogen Laboratory was established and actively utilized for course support, student projects, outreach activities and research. Significant effort has been extended for community education on all levels and establishing effective partnerships with the industry.

Next year, efforts will focus on further refinement of course offerings and laboratory experiences for students. Most of the development will take place in the laboratory, where work is planned for completing the solar installation and student manuals for the equipment. It will also be important to engage in activities which will assure the long-term viability of the Hydrogen and Fuel Cell program at CSULA.

FY 2009 Publications/Presentations

1. Title: Prof._Blekhman-Fuel Cells, Duration: 00:34:08
Link: <http://ess-msite.calstatela.edu/Mediasite/Viewer/?peid=10b36466-a786-43a7-9bfc-142ebc51f5fb>
2. Title: Prof._Blekhman-Hydrogen Economy, Duration: 00:35:24
Link: <http://ess-msite.calstatela.edu/Mediasite/Viewer/?peid=c39fd43a-c9c8-4e95-b799-48ebbf51116f>

References

1. The online summer issue of Cal State L.A. TODAY magazine published an article titled The Next 'Solar' Generation. The article discusses the solar installation by our engineering students including the solar panels for the Zero Emissions Fuel Cell laboratory. The link to the article is <http://www.calstatela.edu/univ/ppa/publicat/today/>
2. Poster explaining the operation of a fuel cell, page 31 of the Lookin' Green Magazine, April 2009. Last retrieved August, 2009. http://www.lookinggreen.com/images/stories/special_edition/LookingGreen200903_31.pdf
3. Cal State LA Advanced Fuel Cell, Lookin' Green Magazine online edition, April 2009. Last retrieved August, 2009. http://www.lookinggreen.com/index.php?option=com_content&view=article&id=343:cal-state-la-advanced-fuel-cell-pg-31&catid=86:special-edition&Itemid=174

X.4 Hydrogen Energy in Engineering Education (H₂E³)

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Contract Number: DE-FG36-08GO18107

Subcontractor:
University of California, Berkeley, Berkeley, CA

Project Start Date: September 15, 2008
Project End Date: September 15, 2011

Objectives

- The Hydrogen Energy in Engineering Education (H₂E³) project is designed to increase awareness of and hands-on experience with hydrogen and fuel cell technology among undergraduate engineering students in California's public universities. H₂E³'s objectives are:
 - to deliver effective, hands-on hydrogen energy and fuel cell learning experiences to a large number of undergraduate engineering students at multiple campuses in the California State University (CSU) and University of California (UC);
 - to provide follow-on internship opportunities for students at hydrogen and fuel cell companies; and
 - to develop commercializable hydrogen teaching tools including a basic fuel cell test station and a fuel cell/electrolyzer experiment kit suitable for use in university engineering laboratory classes.

Technical Barriers

This project addresses the following technical barriers from the Education section (3.9.5) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (D) **Lack of Educated Trainers and Training Opportunities.** Only a small number of universities in California offer hydrogen and fuel cell-specific learning opportunities for undergraduate engineering students. Even at these campuses, the number of engineering faculty with direct experience using fuel cells remains small, and fuel cell course content is underdeveloped.
- (E) **Regional Differences.** California has the advantages of being home to many hydrogen and fuel cell developers and on the leading edge of hydrogen energy infrastructure development. These features call for a special hydrogen energy education effort in California universities that makes use of these existing resources available in close proximity to many campuses.

Contribution to Achievement of DOE Education Milestones

This project will contribute to achievement of the following DOE milestone from the Education section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- **Milestone 21:** Launch new university hydrogen education program (4Q, 2009).

The project supports attainment of the above milestone by creating curriculum, teaching tools, and industry-based learning opportunities that can be replicated by other universities working with industry partners. By the same token, the project also supports completion of Task 5 in the Multi-Year Research, Development and Demonstration Plan: "Facilitate Development and Expansion of College and University Hydrogen Technology Education Offerings," specifically the subtask described as "Work with university partners to develop and expand hydrogen technology course offerings and facilitate networking among schools with similar programs."

Accomplishments

- Established working relationships with faculty from UC Berkeley and Humboldt State University

committed to using H₂E³ curriculum and laboratory equipment in their courses.

- Designed and fabricated 30 benchtop electrolyzer/fuel cell experiment kits and accompanying laboratory activity guides for use in introductory engineering and thermodynamics courses.
- Designed and fabricated two fuel cell test stations capable of operating fuel cell stacks of up to 500 W.
- Began development of written curriculum materials for use in undergraduate engineering courses.

Introduction

A recurring theme in the hydrogen energy field is the unmet need for a new generation of graduating engineers trained specifically in hydrogen and fuel cell energy technologies. The purpose of our project is to help meet this need, specifically in the context of the CSU and UC systems. Together these universities grant over 7,000 engineering degrees each year.

The three-year project, branded as “Hydrogen Energy in Engineering Education” (H₂E³) is being led by the Schatz Energy Research Center (SERC), a unit of the Humboldt State University (HSU) Sponsored Programs Foundation. Our principal partner on the project is the University of California, Berkeley (UCB), represented by their Institute of Transportation Studies (ITS). Industry partners include Jadoo Power Systems, Inc., Protonex Technology Corporation, UTC Power, and IdaTech LLC.

Approach

Adding hydrogen curriculum to existing undergraduate engineering programs is not a trivial task. Engineering departments and the organization that accredits them require students to meet numerous stringent requirements in order to graduate. There is little slack in a typical undergraduate engineering course plan to add new curriculum. In order to add hydrogen education to existing engineering programs, we need to find creative ways to fold it into courses and help instructors meet their existing course objectives.

We are working closely with engineering faculty to develop lesson plans that can be substituted for segments of existing courses, including introductory engineering, introductory and advanced thermodynamics, manufacturing engineering, upper-division engineering laboratory, and in courses on the general topic of energy and society. We are also developing laboratory hardware that the students will be able to use to perform hands-on experiments that reinforce key points covered in the lecture material. The partners on this effort bring

years of relevant experience in teaching about hydrogen energy and developing fuel cell technology.

Results

Our work to date has focused primarily on establishing needed relationships and developing the hardware that will be used for student laboratory activities. At the time of preparing this report we have completed fabrication of 30 benchtop electrolyzer/fuel cell kits and are nearly ready to deploy two fuel cell test stations, which include fuel cell stacks built by SERC.

Working Relationships – We have established a subcontract for \$75,000 with UCB and have consulted extensively with UCB’s principal representative on the project, Timothy Lipman of UCB’s ITS. We held a project kickoff meeting in October 2008 with faculty members from UCB’s mechanical engineering department and secured their support for the project. We also met with engineering faculty and technical support staff at HSU who agreed to pilot H₂E³ curriculum in their courses. Through the Annual Merit Review meeting and other connections, we have identified educators both within and outside the UC and CSU systems who are interested in the H₂E³ project.

Electrolyzer/Fuel Cell Kits – The electrolyzer/fuel cell kits developed for this project are based on an earlier successful SERC design created for use in high school chemistry classes. With this kit, students use electric power to generate hydrogen gas through water electrolysis, then use the hydrogen to power a fuel cell connected to a mechanical load. The kit is instrumented so students can measure the efficiency of each energy conversion step. The new design improves kit performance and allows additional experimental activities such as measurement of waste heat generated during electrolysis (see Figure 1).

Fuel Cell Test Stations – We have completed and tested one of the two test stations to be built as part of this project, with the second station on track for completion during August 2009. The test stations allow the operator to directly observe and record data on a fuel cell stack while adjusting a number of operating parameters, including load current, temperature, air/fuel stoichiometry, and frequency and duration of hydrogen purges (see Figure 2). Each test station is supplied with a 500-Watt, 300 cm² active area fuel cell stack designed and built by SERC. The stacks are internally humidified and water-cooled (see Figure 3). We have completed assembly of both stacks and have tested the first stack, which is performing satisfactorily (see Figure 4 for a current-voltage polarization curve generated during stack testing).

Hydrogen Curriculum – We are creating lesson plans for use in the courses listed above. To date we have completed a lab activity guide for use with the

FIGURE 1. H_2E^3 Electrolyzer/Fuel Cell Kit Showing Component Nomenclature

FIGURE 2. SERC Engineers Commission H_2E^3 Fuel Cell Test Station

electrolyzer/fuel cell kits and are nearing completion of lecture material for a three-week module on hydrogen and fuel cells to be used in introductory engineering courses such as E10 in UCB's mechanical engineering program and ENGR 115 in HSU's environmental

FIGURE 3. 8-Cell Fuel Cell Stack with 300 cm² Active Area

FIGURE 4. Current-Voltage Polarization Curve for Fuel Cell Stack

resources engineering program. We have also identified readings in several textbooks on hydrogen energy to be assigned as part of the curriculum modules under development. To assist with marketing of the H_2E^3 curriculum, we have created a project logo and Web site (www.hydrogencurriculum.org).

Conclusions and Future Directions

The first year of the three-year project has been productive, with the establishment of working relationships with faculty at the two pilot campuses, UCB and HSU, and completion of the bulk of our planned hardware development. In year two we will turn our attention to completing course lesson plans and piloting these lesson plans and associated lab activities in undergraduate engineering classes. We will also deploy the project hardware for use in lab sections of these classes. We will then refine the course materials as needed based on student and instructor feedback. We will work with our industry partners to secure internships for students who have participated in courses that include H_2E^3 material and will monitor outcomes for these interns and their industry hosts. In the final year of the project we will recruit other UC and CSU campuses to participate in the project

and monitor and report on their learning outcomes. Students from these campuses will also have the opportunity to apply for industry partner internships during the project's final year. We will develop and implement a monitoring and evaluation process to determine the success of the curriculum, teaching tools, internships, and our marketing efforts. We will continue to look for relationships with interested educators and the opportunities they bring to share the project's deliverables with a wider audience.

FY 2009 Publications/Presentations

1. Lehman, Peter. "Hydrogen Energy in Engineering Education (H_2E^3)," presentation to 2009 U.S. DOE Hydrogen Program and Vehicle Technologies Program Annual Merit Review and Peer Evaluation Meeting. May 21, 2009, Washington, D.C.

X.5 Hydrogen Education Curriculum Path at Michigan Technological University

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Contract Number: DE-FG36-08GO18108

Project Start Date: September 1, 2008
Project End Date: July 31, 2011

Objectives

The objectives of this project are to educate university students on the advantages, disadvantages, challenges, and opportunities of hydrogen and hydrogen fuel cells within the United States energy economy. In particular, this project will:

- Develop and/or refine courses in hydrogen technology.
- Develop curriculum programs in hydrogen technology.
- Develop modules for core and elective engineering courses.
- Develop modules to supplement commonly used chemical engineering texts.
- Meet all Department of Energy project management and reporting requirements.

Technical Barriers

This project addresses the following technical barriers from the Education section (3.9) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) Lack of Readily Available, Objective, and Technically Accurate Information
- (B) Mixed Messages
- (C) Disconnect Between Information and Dissemination Networks

Contribution to Achievement of DOE Education Milestones

This project will contribute to achievement of the following DOE milestones from the Education section (3.9) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- **Milestone 21:** Launch new university hydrogen education program. (4Q, 2009)

Accomplishments

The accomplishments of this project to date are:

- Two new courses were proposed and approved at Michigan Technological University.
- A minor proposal was approved at Michigan Technological University. Effective April 2009, students can receive an "Interdisciplinary Minor in Hydrogen Technology."
- Nearly two dozen modules were developed to introduce students in core chemical engineering courses to hydrogen and fuel cell technology.
- Example problems have been created as supplementary material to a popular chemical engineering textbook.
- Three oral presentations have been given and one conference proceeding has been published.

Introduction

There is a strong need for a transformative curriculum to train the next generation of engineers who will help design, construct, and operate fuel cell vehicles and the associated hydrogen fueling infrastructure. In this project, we build upon the project-based, hands-on learning that has been a cornerstone of engineering education at Michigan Technological University. This teaching and learning style is supported by the engineering education literature which indicates that

students learn by doing, particularly through team-based interactive projects with a real-world flavor.

This project has resulted in the formation of an “Interdisciplinary Minor in Hydrogen Technology” at MTU. We focus on student centered design projects, and add additional technical material through elective courses, modules for core courses, and textbook supplements. As a final note, aggressive dissemination of the project results will occur through presentations at the annual meetings of several professional societies.

Approach

The ultimate goal for the hydrogen education program should be to establish an educational infrastructure and database of hydrogen and fuel cell related educational materials, particularly projects and problem sets. The efforts of this project support this mission.

At MTU, we have embraced the concept of hands-on learning as the cornerstone of a newly approved “Interdisciplinary Minor in Hydrogen Technology.” Students that obtain this minor are also required to take newly developed elective courses in fuel cells and hydrogen technology. Focusing on a subset of graduates who choose these options is not enough. In order to reach a wider audience at MTU, modules are being developed for the core curricula in chemical engineering, mechanical engineering, and electrical engineering. Each module stands alone and can be assigned to students as an in-class problem, a homework assignment, or a project. The modules use the fundamental concepts taught within the core course and apply them to hydrogen generation, distribution, storage, or use within a fuel cell. Thus, students are able to see the applications of the fundamentals from their courses. Finally, we are creating supplements to two of the most popular chemical engineering textbooks as another way to introduce hydrogen technology and fuel cells to university students.

The core course modules are to be tested throughout the nation. The results of this curriculum project and testing results are to be disseminated through professional societies in chemical engineering, mechanical engineering, electrical engineering, and engineering education. Course materials, modules, and textbook supplements will be available for use by engineering educators worldwide.

Results

Results for Task 1.0, Develop and/or refine courses in hydrogen technology:

- To date, we have created two new courses, “Fundamentals of Hydrogen as an Energy Carrier”

to be taught in fall semesters and “Hydrogen Measurements Laboratory” to be taught in spring semesters. Work is currently underway to prepare the course material. A fuel cell laboratory apparatus was ordered for the laboratory course. The purchase of other laboratory instruments is underway.

Results for Task 2.0, Develop curriculum programs in hydrogen technology:

- A minor proposal was developed and circulated through the curriculum committees at the department, college, and university levels. The proposal for an “Interdisciplinary Minor in Hydrogen Technology” was approved by the university senate and upper administration. Students can now receive this minor effective April 2009.
- During the 2008-2009 academic year, there were several group projects in the “Alternative Fuels Group” Enterprise. This Enterprise consisted of undergraduate students in chemical, mechanical, and electrical engineering, as well as materials science and engineering. Students were in their sophomore, junior, or senior year of study. By participating in the group projects, students earned credit towards their degree and (if desired) towards the new minor mentioned above. Student projects included:
 - Hydrogen Economy at Michigan Technological University
 - Analysis of a Hydrogen Powered John Deere e-Gator (see Figure 1)
 - Design and Economic Analysis of a Fuel Cell/Electric Hybrid Fork Lift
 - Hydrogen Economy for the Upper Peninsula of Michigan (see Figure 2)

FIGURE 1. John Deere e-Gator with Hydrogen Power Plant In Vehicle Bed

Results for Task 3.0, Develop modules for core and elective engineering courses:

- The third task of this project is to develop modules for core courses in chemical, mechanical, and electrical engineering courses. Up to this point, modules have been developed for chemical engineering courses as part of a collaboration between Jason Keith and other faculty external to Michigan Technological University, who are consultants on this project. It is noted that the modules are available online at: http://www.chem.mtu.edu/~jmkeith/fuel_cell_curriculum/.

Results for Task 4.0, Develop modules to supplement commonly used chemical engineering texts:

- We have developed a set of examples to supplement Chapters 2 and 3 of the textbook *Elementary Principles of Chemical Processes* authored by R. M. Felder and R. W. Rousseau and published by Wiley. Each example has at least two problems. The problems are organized in “workbook” format where there are blank spaces for students to insert numbers in order to carry out the solutions. It is noted that this textbook is used in the very first chemical engineering undergraduate course at most universities in the nation. The main emphasis of the course is on engineering problem solving for chemical engineers. Students learn best by solving a large number of problems. This supplement is intended to meet the student’s needs while teaching them about hydrogen technology and fuel cells.

Results for Task 5.0, Project management and reporting:

- To date, three quarterly reports (out of 12) have been submitted. In addition, a Powerpoint presentation was prepared and an oral presentation was given at the Annual Merit Review.

Conclusions and Future Directions

The most significant result of this project to date is the approval of a new minor at Michigan Technological University with title “Interdisciplinary Minor in Hydrogen Technology.” The groundwork is in place to teach new courses in hydrogen and fuel cell technology and to introduce these concepts in the core chemical engineering curriculum at MTU.

Future work will include the following:

- Future work for Task 1.0, Develop and/or refine courses in hydrogen technology: Order experimental units for use in the hydrogen measurements laboratory course; develop laboratory experiments; teach courses.
- Future work for Task 3.0, Develop modules for core and elective engineering courses: Develop modules for core courses in mechanical engineering and electrical engineering curricula; test chemical engineering modules at MTU and other national universities.
- Future work for Task 4.0, Develop modules to supplement commonly used chemical engineering

FIGURE 2. Students in the Alternative Fuels Group Enterprise developed this map of Michigan’s Upper Peninsula showing optimized locations of twelve hydrogen fueling stations. This result was part of a hydrogen economy project with 10% of total vehicles using hydrogen fuel cells.

texts: Finish supplementary material for Felder & Rousseau textbook; begin supplementary material for Geankoplis textbook (*Transport Processes and Separation Process Principles*, published by Prentice Hall, for junior chemical engineering courses).

- Future work for Task 5.0, Project management and reporting: All quarterly and annual reports will be completed on time.

Special Recognitions & Awards/Patents Issued

1. Jason Keith was named trustee of the CACHE Corporation due to his contributions to the chemical engineering modules.
2. A portion of the material developed on this project was used in a special course MEEM4990 Advanced Propulsion for Hybrid Vehicles, which was offered via distance education to unemployed engineers from the automotive industry during spring semester 2009.

FY 2009 Publications/Presentations

1. Oral Presentation: J.M. Keith, D. Chmielewski, H.S. Fogler, V. Thomas, and M. Gross, "CACHE Module Development for Introducing Energy into the Chemical Engineering Curriculum: Fuel Cells," 2008 American Institute of Chemical Engineers Annual Meeting, Philadelphia, PA.
2. Oral Presentation: J.M. Keith, D. Crawl, D. Caspary, J. Allen, D. Meng, A. Mukherjee, J. Naber, J. Lukowski, J. Meldrum, and B. Solomon, "Hydrogen Curriculum Path at Michigan Technological University," 2009 DOE Vehicle Technologies Program Annual Merit Review, Arlington, VA.
3. Oral Presentation: J.M. Keith, D. Crawl, D. Caspary, J. Allen, D. Meng, A. Mukherjee, J. Naber, J. Lukowski, J. Meldrum, and B. Solomon, "Hydrogen Curriculum at Michigan Technological University," 2009 American Society for Engineering Education Annual Meeting, Austin, TX.
4. Conference Proceedings: J.M. Keith, D. Crawl, D. Caspary, J. Allen, D. Meng, A. Mukherjee, J. Naber, J. Lukowski, J. Meldrum, and B. Solomon, "Hydrogen Curriculum at Michigan Technological University," Proceedings of the 2009 American Society for Engineering Education Annual Meeting & Exposition, Austin, TX.

X.6 Bachelor of Science Engineering Technology Hydrogen and Fuel Cell Education Program Concentration

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Contract Number: DE-FG36-08GO18109

Project Start Date: August 1, 2008
Project End Date: December 30, 2009

Objectives

- Prepare students who can successfully work as hydrogen and fuel cell technology (HFCT) professionals in government, industry, and academia.
- Program graduates will demonstrate an appropriate mastery of the knowledge, techniques, skills, and modern tools related to hydrogen and fuel cell technology.
- Program graduates will demonstrate an ability to apply current knowledge and adapt to emerging applications of hydrogen and fuel cell technology.

Technical Barriers

This project addresses the following technical barriers from the Education section (3.9.5) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) Lack of Readily Available, Objective, and Technically Accurate Information
- (F) Mixed Messages

Contribution to Achievement of DOE Education Milestones

This project will contribute to achievement of the following DOE milestones from the Education section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- **Milestone 21:** Facilitate Development and Expansion of College and University Hydrogen Technology Education Offerings. (4Q, 2009)

Accomplishments

- Courses that were developed have been approved by the UCF College of Engineering Curriculum Committee and assigned course numbers as follows:

EGN4300C Hydrogen Production and Handling	3 Credit Hours
EGN4731C Fuel Cell Technologies I	3 Credit Hours
ETM4231 Applied Thermodynamics and HVAC	4 Credit Hours
EGN4730 Renewable Energy Systems	3 Credit Hours
ETM4331 Applied Fluid Mechanics	4 Credit Hours
ETM4220 Applied Energy Systems	4 Credit Hours

- The course ETM4220 Applied Energy Systems has been offered in Spring 2009.
- The following courses are offered to students in Fall 2009:

EGN4731C Fuel Cell Technologies I	3 Credit Hours
EGN4730 Renewable Energy Systems	3 Credit Hours
ETM4331 Applied Fluid Mechanics	4 Credit Hours

- The following course will be offered to students in Spring 2010:

EGN4300C Hydrogen Production and Handling	3 Credit Hours
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Students from all engineering majors and from engineering technology can register for the above courses.

- **Energy Certificate program** based on the current HFCT program has been approved.

Introduction

A program focused on HFCT in the Engineering Technology Department (ENT) jointly with the Florida Solar Energy Center (FSEC) at UCF has been developed. The HFCT Program will support the need for educated graduates that comprise the next generation workforce needed for research, development, and demonstration activities in government, industry, and academia. The efforts include the development and delivery of undergraduate courses at the ENT and FSEC within the ABET-accredited Bachelor of Science (BS) in Engineering Technology program. The mode of course offering will be both in class and on line, which will increase the number of students enrolled. The proposed project facilities are located at the College of Engineering and Computer Science, at FSEC of UCF and at all regional campuses of UCF. The FSEC is a unique component of the proposed effort. FSEC has been conducting hydrogen and fuel cell research for 25 years and has dedicated facilities and a selection of unique laboratory equipment that will be made available to the students for this project.

Current public knowledge and awareness levels of hydrogen and fuel cells are low, however, and prevalent misunderstandings of hydrogen properties have affected negative opinions about the safe use of hydrogen as an energy carrier. The Hydrogen, Fuel Cells & Infrastructure Technologies Education subprogram seeks to facilitate near-term market transformation and future commercialization by providing technically accurate and objective information to key target audiences, including: state and local government representatives, potential end users, safety and code officials, and local communities. Undergraduate and graduate students, professors, and middle and high school teachers and students comprise another important audience, as they are our nation's future researchers, scientists, engineers, technicians, and technology users.

Approach

The approach for achieving the objectives of the project to develop and sustain a BS program in HFCT includes developing the courses for HFCT concentration and utilizing the existing courses to serve the HFCT program. The course offering has started from Spring 2009 by offering ETM4220 Applied Energy Systems. In Fall 2009 three more core courses are offered. These are EGN4731C Fuel Cell Technologies I, EGN4730 Renewable Energy Systems and ETM4331 Applied Fluid Mechanics. Efforts to promoting the program include extensive advertisement, recruiting students and outreach plans, visits to community colleges and other institutions, publications and presentations in professional meetings.

The evaluation of HFCT program will be conducted with help from Program Evaluation and Educational Research Group, an evaluation unit within the College of Education at UCF. The evaluation will engage multiple perspectives, use a wide range of qualitative and quantitative methods, and triangulation procedures to assess and interpret a multiplicity of information. Data will be gathered during all phases of the program to provide timely formative feedback to/from project stakeholders on implementation, participants' perspectives about the activities and what they may have learned, and how goals and objectives are being met. Formative evaluation will provide recommendations and allow for design modifications to improve course impact answering questions like: Is the program providing high-quality experiences? What impact is the program having on participating students' attitude, interest, confidence and knowledge related to hydrogen and fuel cell technology? Is faculty using project-developed content to replace some of their standard lessons?

Results

Courses that were developed have been approved by the UCF College of Engineering Curriculum Committee and assigned course numbers as follows:

EGN4300C Hydrogen Production and Handling	3 Credit Hours
EGN4731C Fuel Cell Technologies I	3 Credit Hours
ETM4231 Applied Thermodynamics and HVAC	4 Credit Hours
EGN4730 Renewable Energy Systems	3 Credit Hours
ETM4331 Applied Fluid Mechanics	4 Credit Hours
ETM4220 Applied Energy Systems	4 Credit Hours

The course ETM4220 Applied Energy Systems has been offered in Spring 2009. This course is taught by Dr. Sleiti as part of the HFCT program. Thirty-seven students have taken the course. The ETM4200 course is both a requirement for ENT as well as an elective course for other engineering programs.

The following courses are offered to students in Fall 2009:

EGN4731C Fuel Cell Technologies I	3 Credit Hours
EGN4730 Renewable Energy Systems	3 Credit Hours
ETM4331 Applied Fluid Mechanics	4 Credit Hours

The following course will be offered to students in Spring 2010:

EGN4300C Hydrogen Production and Handling	3 Credit Hours
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Students from all engineering majors and from engineering technology can register for the above

courses. The courses will be offered to students according to the schedule in Table 1.

The principle investigator (PI) leads the plan to promote the HFCT program and recruit students. It is anticipated that a large number of current UCF students will join the program as the courses are being offered for all engineering majors and engineering technology students.

UCF approval to offer an **Energy Certificate program** based on the current HFCT program has been granted.

The team has started delivering the courses in Spring 2009, which began January 2009. The course ETM4220, Applied Energy Systems, has been offered and taught by the PI, Dr. Sleiti. The following three courses are already scheduled to be offered to students in Fall 2009 and Spring 2010:

EGN4300C Hydrogen Production and Handling	3 Credit Hours
EGN4731C Fuel Cell Technologies I	3 Credit Hours
EGN4730 Analysis of Renewable Energy Systems	3 Credit Hours
ETM4331 Applied Fluid Mechanics	4 Credit Hours

The project director is coordinating the work of the team, following up with the college curriculum committee at UCF, communicating with school districts, community colleges and potential partners from industry, and submitting progress reports to the DOE program manager.

Conclusions and Future Directions

It is concluded that the HFCT program is a unique program that will support the need for educated graduates that comprise the next generation workforce needed for research, development, and demonstration activities in government, industry, and academia.

The plans for the future directions are:

- Continue offering the courses for the HFCT concentration.
- Evaluate courses offered.
- Continue working on promoting the program and recruiting students.
- Attend seminars and meetings to disseminate program results.
- Conduct visits to community colleges, school districts and industries.
- Prepare and present technical papers.

FY 2009 Publications/Presentations

1. A.K. Sleiti, "Bachelor of Science Engineering Technology Hydrogen and Fuel Cell Education Program Concentration", presentation at the 2009 DOE Hydrogen Program Merit Review and Peer Evaluation Meeting, Arlington, Virginia, May 21, 2009.
2. A.K. Sleiti, "Bachelor of Science - Engineering Technology Hydrogen and Fuel Cell Education Program Concentration", ASME 2009 International Mechanical Congress and Exposition (IMECE) IMECE2009-12314, November 13-19, 2009, Lake Buena Vista, FL, USA.

TABLE 1. Course Schedule

Course Title	2008-2009			2009-2010			2010-2011			2011-2012			2012-2013		
	SU	F	S	SU	F	S	SU	F	S	SU	F	S	SU	F	S
ETM4220 Applied Energy Systems			X			X			X			X			X
EGN4300C Hydrogen Production and Handling						X		X			X			X	
EGN4731C Fuel Cell Technologies I					X			X			X			X	
ETM4331 Applied Fluid Mechanics					X			X			X			X	
ETM4231 Applied Thermodynamics and Heat Transfer						X			X			X			X
EGN4730 Analysis of Renewable Energy Systems					X			X			X			X	
EGN4XXXC Hydrogen Applications								TBD			TBD			TBD	
EGN4XXXC Fuel Cell Technologies II								TBD			TBD			TBD	

TBD – to be determined

X.7 Development of a Renewable Hydrogen Production and Fuel Cell Education Program

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Contract Number: DE-FG36-08GO18110

Project Start Date: August 1, 2008
Project End Date: July 30, 2011

For the purposes of this grant, the terms hydrogen-based technologies, hydrogen energy and hydrogen education are used broadly to include the production, transport, storage, and utilization of hydrogen. This includes both electrolysis and fuel cell applications.

Technical Barriers

This project addresses the following technical barriers from the Education section (3.9) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) Lack of Readily Available, Objective, and Technically Accurate Information
- (B) Mixed Messages
- (C) Disconnect Between Hydrogen Information and Dissemination Networks
- (D) Lack of Educated Trainers and Training Opportunities

Objectives

The objective of this project is to develop a comprehensive university level education program that will:

- Provide exposure to the basics of hydrogen-based technologies to a large number of students. This exposure will provide a level of training that will allow students to converse and work with other scientists and engineers in this field. It will also serve to spark a level of interest in a subset of students who will then continue with more advanced coursework and/or research.
- Provide “mid-level” training to a moderate level of students. More detailed and directed education will provide students with the ability to work to support industry and government development of hydrogen technologies. This level of training would be sufficient to work in the industry, but not be a leader in research and development.
- Provide detailed training to a smaller subset of students with a strong interest and propensity to make significant contributions to the technology development. These individuals will have extensive hands-on experience through internships that will allow them to play a major role in industry, government, and academia.

Contribution to Achievement of DOE Education Milestones

This project will contribute to achievement of the following DOE milestones from the Education section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- **Milestone 21:** Launch new university hydrogen education program. (4Q, 2009)

Accomplishments

- Three new case studies targeting 1) freshman introductory engineering courses, 2) chemical engineering mass and energy balances, and 3) chemical engineering thermodynamics are under development for use in the Fall, 2009.
- The course content in EE 522-Renewable Energy Systems, taught Fall 2008 was modified to increase the content related to fuel cells and electrolysis.
- Two new courses will be offered during the 2009-2010 academic year. The first course will cover hydrogen production and storage. The second course will focus on hydrogen utilization.
- Two undergraduate students have been placed for internships as the Energy & Environmental Research Center's National Center for Hydrogen Technology.

- Two new experimental setups were designed and implemented into chemical and electrical engineering undergraduate laboratories.
- The student organization, PowerOn, developed experiments that will be incorporated into a mobile laboratory that will be taken to middle schools as a part of a program to stimulate interest in science, technology, engineering, and mathematics (STEM) areas.

Introduction

The basic concept of the project is to introduce hydrogen education to a broad distribution of students through the use of structured case studies and experiments that are built into the students required coursework. This guarantees that all undergraduate students in the program will be exposed to the technologies. This level of exposure should generate interest in a subset of these students who would then be interested in taking full semester courses related to hydrogen technologies. This will provide a significant cohort of students that will have a good understanding of the basics making them candidates for entry level jobs in hydrogen-related industries. A smaller subset of these students showing strong interest and aptitude will participate in directed research and internships to produce Bachelor of Science, Master of Science and doctorate graduates that will play a major role in the future development of the hydrogen technology. UND's distance education experience will be used to reach a large and widely dispersed group of students.

Approach

UND is taking advantage of existing infrastructure and programs to provide a comprehensive renewable hydrogen production and fuel cell education program. This program is comprehensive from the standpoint of the level and number of students that will be involved in the program. It is designed to provide multi-discipline formal training to both undergraduate and graduate level engineers and scientists. This will be accomplished by developing case studies that will be implemented into classes through all four years of the undergraduate curriculum. These case studies will be broadly disseminated through the National Center for Case Studies in the Science Teaching Web site making them available to any school in the United States. Two new classes will be generated that will be offered as technical electives at the undergraduate and graduate level. In addition to our on-campus students, the undergraduate class will also be offered through our Distance Education Degree Program (DEDP) to provide access to hundreds of off-campus students across the country and other

nations. UND's DEDP program is the nation's only ABET Engineering Accreditation Commission accredited undergraduate engineering program. Several new hydrogen-related student experiments will be added to our undergraduate laboratory sequence to provide hands-on experience for our students. Additional hands-on experience will be available to selected students through our on-going research at UND, and through summer intern programs to be established with the National Renewable Energy Laboratory (NREL) and Distributed Energy Systems (designer and manufacturer of proton exchange membrane [PEM] hydrogen production systems). UND will develop a hydrogen seminar, bringing in experts in the field from NREL and Distributed Energy Systems to present to UND students. Internships and research opportunities are also available for students at the UND Energy & Environmental Research Center (EERC).

This program is designed to provide an introduction of hydrogen energy to a large number of students, both on and off the UND campus through the case studies and student laboratories. It will provide more detailed training on the topic to a smaller, but still significant group of students through two new courses that will be added to our curriculum and offered through our distance program. In-depth training will be provided to a select group of undergraduate and graduate students through in-house research and internships with the EERC, NREL, and Distributed Energy Systems. We feel this approach will provide high quality students with the exposure of hydrogen energy required to support research, development, and demonstration activities in the government, industry and academia sectors.

Results

Work was initiated to develop three new case studies. These will target 1) freshman introductory engineering courses, 2) chemical engineering mass and energy balances; and 3) chemical engineering thermodynamics. These case studies will serve to introduce all chemical and electrical engineering students at UND to the basics of hydrogen and fuel cell technology.

A new course is under development that will cover hydrogen production and storage. Topic areas include an overview on "why hydrogen" followed by sections on hydrogen production from fossil fuel and biomass, hydrogen from water, and hydrogen distribution and storage. The current texts that are being adopted for the course are "Hydrogen Energy: Challenges and Prospects" by Rand and Dell, and "Hydrogen Fuel: Production, Transport and Storage" edited by R. Gupta. An outline has been developed and work was initiated on developing the first teaching modules.

During the past year, the school has encouraged the development of hydrogen-based projects for the senior

capstone design course. The Renewable Hydrogen Electrolyzer project focused on taking energy from a renewable source, and storing that energy in the form of hydrogen to later be used in a fuel cell. To do this an alkaline electrolyzer was designed and built to produce hydrogen through the process of electrolysis. The overall project goal was to integrate the electrolyzer with an existing wind and photovoltaic power supply, and deliver produced hydrogen to a miniature fuel cell car. Figure 1 depicts the overall system, where the electrolyzer was the system being developed for this project.

The goal of a second project, Combining Alternative Energy Power Sources, was to combine and control the output of unregulated direct current (DC) sources such as fuel cells into a single regulated output to match the load. The purpose of combining sources is to increase the usefulness of alternative energy fuel cell generators which commonly produce unregulated DC output. The solution proposed utilizes a DC to AC (alternating current) converter, a multi-winding transformer, and an AC to DC inverter. In a three-stage system the incoming DC is converted via a full H-bridge to AC, where it is then passed over a two input one output transformer. The power combines in the magnetic spectrum on the transformer core, and the output of the transformer is then converted back into a single DC output. A copy of the circuit design is presented in Figure 2.

FIGURE 1. System overview of renewable power system designed as a senior capstone project.

During the fall 2008 semester, students from EE 522 performed experiments using a Hydro-Geniuses laboratory experimental setup. This equipment contains a solar cell, a single cell PEM electrolyzer, two single cell PEM fuel cells, and a small resistive load. Students generated the current-voltage characteristic curves of the fuel cell and the electrolyzer and analyzed system efficiencies. The two fuel cells were operated both in series and in parallel. During the spring 2008 semester, students from ChE 332 performed experiments using the Hydro-Geniuses laboratory experimental setup. Students generated the current-voltage characteristic curves of the fuel cell and the electrolyzer and analyzed system efficiencies. In this lab, the students are given a memo from their “boss” asking them to design a system to supply 100 kW of electricity. The students need to determine system efficiencies and power curves to propose a design to their boss.

Two new experimental setups were purchased from Heliocentrics. The HP 600 includes a 600 watt water-cooled PEM fuel cell stack, a DC/DC and DC/AC converter, metal hydride storage kit, electric load, and an integrated control system. The off-grid instructor includes a 40 watt fuel cell with integrated microprocessor, electronic load, metal hydride storage, and the constructor kit. A set of laboratories has been developed that will be implemented in to the undergraduate curriculum during the 2009-2010 academic year. Photos of the equipment are given in Figure 3.

Two undergraduate students have been placed for internships as the EERC’s National Center for Hydrogen Technology.

Nilesh Dale, PhD candidate, successfully defended his thesis entitled “Characterization of PEM Electrolyzer and PEM Fuel Cell Stacks using Electrochemical Impedance Spectroscopy” in November 2008. Mr. Dale presented an open seminar on his work to

FIGURE 2. Circuit design developed as a part of senior capstone project to combine and control output of unregulated DC sources (fuel cells) into single regulated load to match load.

FIGURE 3. Laboratory Experiments in Hydrogen Utilization

undergraduate chemical and electrical engineering students.

The student organization, PowerOn, is developing experiments that will be incorporated into a mobile laboratory. This mobile laboratory will be taken to middle schools as a part of a program to stimulate interest in STEM areas. As a part of this DOE program several undergraduate chemical engineering students have developed suitable laboratories on hydrogen production and utilization. Implementation of the PowerOn program will be performed under a separate grant, and is not a part of this project. Undergraduate students also used these experiments as a part of UND's Young Engineers Summer Camp focused on grades fourth through eighth.

Conclusions and Future Directions

To date this project has impacted approximately 60 students, primarily through the laboratory experiences. When fully implemented, it is expected that approximately 200 students per year will be exposed to case studies and laboratories at UND. A group of approximately ten students have been fully immersed in hydrogen technology through the capstone design experience.

During the next year work will continue on development of additional case studies. The case studies will be published to provide national access. Work will continue on the development and delivery of the new courses. Additional experiments and demonstrations will be developed for the new equipment. Recruitment and placement of additional internships will be undertaken. Efforts will be made to bring in an outside speaker for the hydrogen seminar.

FY 2009 Publications/Presentations

1. Development of a Renewable Hydrogen Production and Fuel Cell Education Program presented at the 2009 U.S. DOE Hydrogen Program and Vehicle Technologies Program Annual Merit Review and Peer Evaluation Meeting.

X.8 Dedicated To The Continued Education, Training and Demonstration of PEM Fuel Cell Powered Lift Trucks In Real-World Applications

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Contract Number: DE-FC36-08GO18105

Subcontractor:

Hydrogenics, Mississauga, Ontario, Canada

Project Start Date: September 1, 2008

Project End Date: August 31, 2011

Objectives

Through both the education and deployment segments of the project, the objective has been to build further upon LiftOne's successful 2007 fuel cell lift truck deployment in South Carolina by:

- Educating a broad and key group of stakeholders to the benefits of fuel cell and hydrogen technology including, facilities management, operators, maintenance personnel, health and safety groups, first responders, authorities having jurisdiction, technical and community colleges and the general public.
- Demonstrate fuel cell and hydrogen technology through one-month long and geographically diverse deployments of two hydrogen fuel cell-powered lift trucks in real-world applications involving large, prominent companies.
- Demonstrate further this technology by bringing the fuel cell-powered lift trucks to additional high profile public sites.
- To further assist in the commercialization of fuel cell and hydrogen technology through the successful deployments and presentation of cost value propositions.

Technical Barriers

This project addresses the following technical barriers from the Education section (3.9.5) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (B) Mixed Messages
- (E) Regional Differences

Contribution to Achievement of DOE Education Milestones

This project will contribute to achievement of the following DOE milestones from the Education section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- **Milestone 14:** Hold Community Seminars to introduce local residents to hydrogen (4Q, 2009). This has been done through the H2 -101 Education Sessions held during the first eight months, by engaging with first responders, engineering groups, companies and individuals at shows and public demonstrations, including the 2009 National Hydrogen Association (NHA) Conference.
- **Milestone 18:** Develop end-user workshop materials for use at events (4Q, 2009). LiftOne has shown the hydrogen fuel cell-powered lift trucks at all education sessions conducted at the LiftOne branch locations and handed out versions of the lesson plan to the attendees, comprised of lift truck fleet users. Additionally, through the actual site deployments, end-users at companies such as Stanley Tools, Lowe's, Bausch & Lomb, Michelin Tire, Electrolux and UTi have and will continue to be introduced to hydrogen fuel cell-powered lift trucks.
- **Milestone 19:** Develop short courses for end-users at technical colleges (4Q, 2011). LiftOne has engaged with several regional community colleges during the past year and made arrangements to make H2-101 presentations. LiftOne did conduct two hydrogen seminars at the North American Council of Automotive Teachers - 2009 Conference held at Central Piedmont Community College – North Campus, on July 22–23.
- **Milestone 23:** Hold teacher workshops (2Q, 2007 through 4Q, 2010). Through the above-mentioned North American Council of Automotive Teachers Conference, LiftOne was able to connect with several Charlotte, NC area high school technical

instructors to make arrangements for future on site hydrogen workshops.

- **Milestone 29:** Evaluate knowledge and opinion of hydrogen technology of key target audiences toward meeting objectives (4Q, 2009). Each Hydrogen Education Session held has included initial assessments of hydrogen awareness among the attendees.

Accomplishments

- Designed and presented a comprehensive Hydrogen “101” seminar, which has increased overall hydrogen awareness in LiftOne’s NC-SC-VA region. Focusing on proton exchange membrane (PEM) fuel cells for the material handling industry, the one-day sessions have been held among a wide variety of lift truck fleet users at the LiftOne seven branch locations.
- Demonstrated fuel cell-powered trucks at high profile events such as the ribbon cutting ceremony for the Columbia, South Carolina Hydrogen Fueling Station; the NHA Conference and at Michelin Tire’s Corporate “Earth Day.” These events provided prime opportunities to evidence the immediate commercial availability of hydrogen fuel cell power for sit-down rider (Class I) electric lift trucks (Figure 1).
- Successful launching of the six-site deployment schedule in May, with the first site at Stanley Tools, where the two fuel cell-powered lift trucks were put into full service. End users are introduced to the benefits of hydrogen fuel cell power, with hands-on experience in both operation and refueling.
- Compiled data from the Hydrogenics HyPX Fuel Cell Power Packs, along with the Air Products HF-150 mobile fueller, and submitted the data to the National Renewable Energy Laboratory for analysis.

FIGURE 1. LiftOne Truck Fueling at the Columbia, SC, Hydrogen Station

Introduction

The materials handling industry, a \$12 billion global market representing approximately 750,000 lift trucks sold each year, has proven to be a significant near-term market for PEM fuel cell adoption in a mobility application. This is due to the lack of emissions and the increased productivity the technology provides vs. that of using lead-acid batteries or fossil fuels (propane, gasoline, diesel) for lift trucks and other material-handling units. As a leading dealership in the Carolinas and Virginia, LiftOne first demonstrated PEM fuel cells in 2007, and was able to gain early field trial experience, while recognizing the acute overall need for hydrogen education. To help facilitate the integration of hydrogen fuel cells into real-world applications in the material handling industry, LiftOne first developed a comprehensive hydrogen education and awareness presentation. The seminar is conducted for lift truck users at LiftOne branches, and other sessions are held for selected technical colleges and professional industrial organizations. The sessions began in late March and have made a positive impact on increasing hydrogen awareness. The deployment segment of the project commenced in mid-May with the two fuel cell-powered lift trucks put into full service for one-month long periods at strategically selected high profile companies. The exposure gained by the deployments has and will continue to be a tremendous method of demonstrating the viability of hydrogen fuel cell power. LiftOne also participated by displaying the fuel cell lift trucks at the NHA Conference held in Columbia, SC, from March 30th through April 3rd, which had over 2,500 people in attendance.

Approach

Recognizing the need to help increase hydrogen awareness among material handling users, LiftOne’s approach for hydrogen education has been focused primarily on the identification of key target audiences. This has been the strategy for both the education and deployment segments of the project. On the education side, the seminar content was designed for the layman’s introduction to hydrogen; its history and use over time, and its associated properties/safety items. Fuel cell design and applications, with a strong focus on material handling applications for fuel cells are the key components of the free seminar’s content. A live demonstration of a working fuel cell in an electric forklift ends each 4-5 hour session. The target audience includes representatives from companies operating medium to large electric material handling fleets, with a secondary audience from fossil fuel powered fleets. Individuals and technical colleges are a third audience, with the

entire effort geared toward providing overall hydrogen education awareness, while at the same time providing substantial evidence to allow companies to further progress in the investigation of this alternative fuel.

For the LiftOne deployment segment, a selection criterion was established to determine six optimum trial sites for the two fuel cell-powered CAT® lift trucks for one-month long periods each. These included larger, high profile companies with sizable electric fleets, running multiple shifts and providing high hour usage. For each site, a complete presentation was made and a proposal made for the trial scenario. Upon selection, a survey was made for the correct siting of the mobile fueler. Full orientation classes are conducted with the operators and other deployment site personnel, with hydrogen safety training, fuel cell operation training and hands-on training for the mobile fueler. Once underway, LiftOne monitors fuel cell performance, interacts with site personnel and downloads data. After the conclusion of the trial, the data is compiled, analyzed and then presented at the review meeting with the company participating in the deployment. A critical item at the meeting is the value proposal, which highlights the cost of fuel cell operation vs. that of lead-acid batteries. All the cost components for fuel cell integration into fleets are reviewed, as well as the budget information previously furnished by that site's management. From this point, the recommendations can be made and when justified, the ultimate steps taken toward a more involved "pilot" program.

Results

Positive progress has been seen for both the segments of the LiftOne project. To assist in increasing the overall hydrogen awareness level in the material handling industry, nine hydrogen education seminars were conducted at LiftOne branch locations. Over 90 key end-users have participated in these sessions thus far (Figure 2). The demonstration of the working fuel cell in a lift truck at the sessions provided the attendees an opportunity to see what had previously only been read about. Additional awareness and exposure for the fuel cell powered lift trucks was gained through demonstrations at strategic events. Most notably, the trucks were exhibited at the NHA's 2009 Conference in Columbia, SC, in April, where over 2,500 attendees were able to view the functioning units. During this event, the fuel cell-powered lift trucks appeared on a local television station's morning show, participated in the conference "live demo" area, and were actually utilized for moving materials prior to the start by the set-up company. LiftOne was also able to participate in the ribbon cutting ceremony at the newly commissioned Columbia, SC, hydrogen fueling station on March 31st. The project's three fuel cells were all fueled at this station.

FIGURE 2. LiftOne H2 – Education Session Attendees

Progress was also seen through the positive engagement with several local community and technical colleges. Specifically the interaction with Central Piedmont Community College - North Campus in Huntersville, NC, led to LiftOne's participation in the North American Council of Automotive Teachers - 2009 Conference. At the conference attended by 250 college instructors, two presentations and a demonstration of a working fuel cell were given. LiftOne has been able to supplement its hydrogen awareness campaign, by reaching out to this important technical sector of the education community.

With regard to the deployment segment of the project, significant progress was made through the engagement and subsequent approvals to schedule the actual deployments at six large, high profile electric lift truck fleet users. These companies are: Stanley Tool, Lowe's, Michelin Tire, Bausch & Lomb, Electrolux and UTi. A critical result involved the successful interaction with all of these major companies, most with multiple locations across the United States. These opportunities allowed LiftOne to make full presentations providing the necessary initial educational information covering hydrogen, PEM fuel cells and the justification for real-world applications in the material handling industry.

As of this report, we have completed the successful deployment at Stanley Tools at their one million+ sq. ft. distribution center. The units were put into regular service among the facility's 100+ lift truck fleet, with over 10 operators and additional management personnel participating in the trial. The review meeting is pending as of the date of this annual report, and will be held the week of August 17th. Positive results were experienced as the fuel cell powered trucks performed well and were able to handle all tasks efficiently and effectively with virtually no issues. Operators easily adapted to the mobile fueler and were able to handle the procedure with no difficulties at all. Most weeks evidenced between four and 11 fills each per fuel cell,

accomplished during Stanley Tool's five-day/two-shift work schedule (Figure 3, Figure 4).

Conclusions and Future Directions

A critical realization has been made during our efforts over the first year. Specifically, regarding the high level of intrigue that exists surrounding the practical use of hydrogen fuel cells for powering lift trucks. This has been seen to be true among companies operating all sizes and styles of fleets. LiftOne has been able to address much of the intrigue through both the project's education segment and with the start of the deployment segment. Increased awareness and comprehension of hydrogen use as a fuel has resulted, while many of these companies have evidenced a willingness to further investigate this clean energy alternative to battery power. In this respect, LiftOne was able to positively engage with several major companies where historically there

was no such engagement, exclusively through the topic of hydrogen fuel cells.

The following conclusions have been derived through the LiftOne Hydrogen Project's first year:

- There is an unquestionable, acute willingness to investigate and learn more about fuel cell power among the majority of companies that operate material handling fleets.
- LiftOne's ability as a lift truck dealership to provide hydrogen education to companies at the local level has been positive, by increasing awareness of this technology to a variety of end users. Showing the actual working fuel cell-powered unit has been a huge benefit.
- A strong desire definitely exists at this time, for correct sized companies to consider the practicality and economical viability of using hydrogen fuel cells for their lift trucks.
- Actual deployments are an absolute necessity for "next step" fuel cell consideration.

As far as future direction for the LiftOne hydrogen project, these steps will be undertaken:

- Continue to revise the education session's content as deemed necessary, incorporating fuel cell technology developments and cost model improvements.
- Expand the education portion further through increased engagement with more local community and technical colleges.
- Continuation of engagement with first responders through their inclusion at all deployment orientation sessions.
- Maximize local and national publicity of the lift truck deployments through newspapers, television and trade publications.

FIGURE 3. Fuelings For Fuel Cell # 11 in Truck # 0264 LiftOne – Site # 1

FIGURE 4. Fuelings For Fuel Cell # 18 in Truck # 0265 LiftOne – Site # 1

FY 2009 Presentations

1. Bill Ryan, General Manager / VP - LiftOne, "Emerging Markets", Keynote Session 4, National Hydrogen Association Conference and Hydrogen Expo, Columbia, South Carolina on April 1, 2009.
2. Tom Dever, Hydrogen Education Program Director - LiftOne, "Dedicated to the Continued Education, Training and Demonstration of PEM Fuel Cell Powered Lift Trucks in Real-World Applications", US Fuel Cell Council Spring Meeting, Arlington, Virginia on May 20, 2009.
3. Tom Dever, Hydrogen Education Program Director and Chris File, Technical Trainer - LiftOne, "Hydrogen PEM Fuel Cells In The Material Handling Industry", North American Council of Automotive Teachers – 2009 Conference, Central Piedmont Community College - North Campus, Huntersville, North Carolina, July 22-23, 2009.

X.9 Hydrogen Education in Texas

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Contract Number: DE-FC36-08GO18112

Subcontractor:
Texas H2 Coalition, The Woodlands, TX

Project Start Date: August 1, 2008
Project End Date: September 1, 2010

Objectives

- Project Aim: Increase basic knowledge and awareness of Texas state and local government leaders about hydrogen and fuel cell technologies.
- Project Objectives:
 - Establish communications to reach the target audience.
 - Assemble needed materials for education and outreach.
 - Conduct workshops and webinars for the five major Texas cities/regions.

Technical Barriers

This project addresses the following technical barriers from the Education section (3.9) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) Lack of Readily Available, Objective, and Technically Accurate Information
- (C) Disconnect Between Hydrogen Information and Dissemination Networks
- (E) Regional Differences

Contribution to Achievement of DOE Education Milestones

This project will contribute to achievement of the following DOE milestones from the Education section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- **Milestone 17:** Hold Hydrogen 101 Seminars (4Q, 2008 through 4Q, 2012)

Accomplishments

- Expanded Texas e-mail hydrogen/fuel cell contact list.
- Initiated discussions with regional contacts, including Clean Cities' coordinators.
- Conducted outreach and education activities including two briefings (Austin and Houston) and displays at two conferences (Dallas/Ft. Worth and Houston).
- Presented project at the DOE 2009 Annual Merit Review.
- Completed initial Web site design.
- Assembled basic educational materials, including information on Texas and hydrogen.
- Began compiling baseline awareness information.

Introduction

Between 2000 and 2004, Texas demonstrated considerable interest and activity related to hydrogen and fuel cell technology. During that time, the Houston Advanced Research Center (HARC) organized a fuel cell consortium and created a fuel cell testing lab. Interest and activities have declined in Texas since 2004. In 2008, in cooperation with the Texas H2 Coalition and the State Energy Conservation Office, HARC developed the *Texas Hydrogen Roadmap*. It was apparent from analysis conducted for this report that Texas has significant advantages for hydrogen and fuel cell, but there is relatively little activity within Texas compared with other key states. The provision of informational materials and activities through outreach and education was seen as an effective way of reaching decision makers in Texas. Previous hydrogen/fuel cells efforts by the state and the Texas H2 Coalition had targeted the five major Texas urban areas, and this same targeting approach was adopted for this project.

Approach

The overall approach for this project takes advantage of HARC's experience in energy and air quality programs to conduct outreach and education efforts to reach state and local government leaders. Many of these people know of HARC and are located in the five largest metropolitan areas (Figure 1). In addition, the Texas H2 Coalition had worked in most of the target cities to explore hydrogen and fuel cell projects. The outreach and education activities that were identified for this project include establishing communications with key organizations in these areas (particularly Clean Cities), compiling contact information on the target audience, and conducting workshops and briefings to communicate hydrogen and fuel cell education information. These activities are being organized, whenever possible, in coordination with other metro area events and activities.

Results

The major results to date on this project have been (1) establishing key contacts in each of the target regions and (2) determining initial schedules for hydrogen education workshops. Based on discussions with other

state hydrogen education programs, it was important to coordinate workshops with key organizations in target areas to best meet the target audience. The workshop format was revised to be shorter in duration with more opportunities for follow-up activities such as briefings to identified individuals or groups.

Educational materials developed by DOE and other organizations have been reviewed by project staff to determine how they could be utilized. One page flyers on each topical areas are being provided to participants and as part of the website. A limited number of links to key educational materials and sites is also included in the Web site design to attempt to refer the target audience to the most relevant, accurate, and informative information sources (for example, DOE's hydrogen code training Web site). HARC had previously published the *Texas Hydrogen Roadmap* working with the State Energy Conservation Office and had compiled Texas-relevant information that could be used for outreach and education. Some of these materials are incorporated in presentation materials. In addition, HARC has identified current hydrogen fuel cell applications in Texas (fuel cell forklifts, backup power for cell towers, and fuel transit bus) to use as real world examples in outreach and education.

FIGURE 1. Target Regions and Application Examples

As an example of coordinative activities, HARC has identified a joint opportunity with the National Renewable Energy Laboratory's (NREL's) hydrogen code training workshop. HARC worked with NREL staff and contractors to establish a date and meeting place for these two events to occur over a two day period. This enables local government staff to help publicize and recruit participants for these related events. HARC has been involved in a previous project with area government staff on alternative fuels for the regional airport facility. The area has been considering hydrogen fuel cells as one of their options of interest for potential application at the airport and in related activities at or near the airport. The new fuel cell forklifts that are to be located in the San Antonio area serve as a real world example for workshop participants.

Following discussions with various organizations, workshop dates and venues have been identified for the Houston and Austin areas. The Houston event is planned to occur at the same location as two events that reach the target audience, one conference on air quality and the other on energy. In all target cities, HARC will work with Clean Cities' coordinators to communicate with the target audience.

The project has sought ways to assess progress on improving basic knowledge of hydrogen and fuel cells. Toward this end, questions are being posed as part of briefings and outreach to roughly assess the current level of knowledge of the target audience. Topic areas from the DOE's hydrogen education surveys are being used for this purpose to help establish a rough baseline. Follow-up assessments will be used with workshop participants to gauge progress. This is not intended to be a test/post test survey process, but a rough guide to improving materials and messages in the workshops, as well as improving information on the Web site.

Finally, incentives are being evaluated that would help ensure active participation in Texas workshops and briefings. Examples of incentives include a technology prize (such as a solar flashlight or fuel cell science kit), scholarships for hydrogen continuing education credits, training certificates, and/or provision of a conference registration fees.

Future Directions

- Workshops dates and venues will be finalized and workshops implemented.
- Additional opportunities for briefings to target audience will be identified.
- Target audience contacts will continue to be expanded.
- Project Web site will be launched.

FY 2009 Publications/Presentations

1. Texas and Hydrogen: Hydrogen 101; Houston Clean Cities Stakeholders Meeting; Houston-Galveston Area Council; March 18, 2009.
2. Texas and Hydrogen: Hydrogen 101; briefing for Texas legislative staff; Austin, Texas; April 9, 2009.
3. Hydrogen Education in Texas: DOE Annual Merit Review, May 21, 2009.

X.10 Development of Hydrogen Education Programs for Government Officials

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Contract Number: DE-FG36-08GO18113

Subcontractor:

Scott Greenway, Greenway Energy, Aiken, SC

Project Start Date: October 1, 2008

Project End Date: September 30, 2011

Objectives

- Synthesize objective and technically accurate information that will be made available to a wide audience through the Internet, a national meeting, and training sessions.
- Design and develop educational programs that will clarify the benefits and challenges of moving to a hydrogen economy that avoid over-selling hydrogen technologies.
- Leverage relationships with project team organizations in South Carolina to deploy hydrogen education materials to government and code officials.
- Train a group of hydrogen educators at the project team institutions (The South Carolina Energy Office, The State Fire Marshal's Office, the SCHFCA and Greenway Energy) who will be resources on hydrogen and fuel cells to the target audiences.

Technical Barriers

This project addresses the following technical barriers from the Education section (3.9.5) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) Lack of Readily Available, Objective, and Technically Accurate Information
- (B) Mixed Messages
- (C) Disconnect Between Hydrogen Information and Dissemination Networks
- (D) Lack of Educated Trainers and Training Opportunities
- (E) Regional Differences
- (F) Difficulty of Measuring Success

Contribution to Achievement of DOE Education Milestones

This project will contribute to achievement of the following DOE milestones from the Education (3.9) section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- **Milestone 17:** Hold "Hydrogen 101" seminars. (4Q, 2008 through 4Q, 2012)

Accomplishments

- Created 97 slides and four class demonstrations for use as needed based on the interests of the particular audience being addressed. The materials created were based on audience tastes as indicated by project partner representatives.
- Reached 120 state and local government officials and decision makers.

Introduction

Hydrogen and fuel cell technologies are moving out of the laboratory and into economically competitive niche markets such as cell phone tower back-up power and forklift operations. As hydrogen technologies become competitive in these early markets, communities will need to be educated about the opportunities afforded by hydrogen technologies and about safety concerns associated with them.

South Carolina is among a small, but growing, number of states that have a hydrogen implementation strategy and is on the leading edge of fuel cell research and adoption. In order to maximize the resources existing in the state and surrounding region, it is imperative that an effective outreach and education program be conducted so that the decision to accept hydrogen technologies in the local community is informed and wise.

Approach

The project team is composed of South Carolina-based hydrogen experts with connections to technically accurate information; and, civic organizations and associations with the communications networks and events with our target audience already established. The entire team works together to identify specific messaging that the local audience and sub-audiences are interested in. Based on the feedback we gather from the civic organizations and other community opinion leaders, education materials and demonstrations are developed.

The marketing of the project is conducted through the existing Web sites, e-mail distribution lists and communication networks. The distribution of the material is primarily conducted at events associated with each of the civic associations partnered on the project, however, several stand-alone events and webinars are planned.

Results

Q4 2008

- Task 1. State and Local Government Officials Education
 - Subtask 1.1 - Assess, Design, Develop, Implement and Evaluate (Year 1)
 - Discussions with project partners and additional relevant groups identified broad areas of interest to the local target audience. This information was used to focus the development of materials.
 - Design of hydrogen education modules for local officials began in municipalities that are interested in the opportunities presented by hydrogen and fuel cell technologies.
 - These modules present an introduction to hydrogen technologies, show examples of how they are used and demonstrate the competitive advantages in niche applications such as material handling and telecommunications back-up power. The modules are also meant to provide an educational foundation so that local government officials can understand how hydrogen related state initiatives can benefit their region.
- Task 2. Hydrogen Education for Codes Officials
 - Subtask 1.1 - Assess, Design, Develop, Implement and Evaluate (Year 1)
 - Currently, the SCHFCA is working with DOE/ National Renewable Energy Laboratory (NREL) to host a Codes Workshop in conjunction with the National Hydrogen Association (NHA) conference in Columbia in March 2009. During the session with the DOE, training materials for codes officials will be discussed.

Q1 2009

- Task 1. State and Local Government Officials Education
 - Subtask 1.1 - Assess, Design, Develop, Implement and Evaluate (Year 1)
 - The initial project presentation was conducted in February hosted at the Municipal Association of South Carolina (MASC). This session focused on officials within the municipal government system in South Carolina. The MASC, a project partner, provided meeting space and assisted in marketing the project to its members.
 - A trial webinar was conducted on March 24th one week prior to the NHA Conference in Columbia and was intended to provide state and local government officials that were planning on attending the NHA Conference with adequate background knowledge prior to their arrival at the convention.
 - A presentation was given at the 2009 NHA Conference highlighting the objectives and accomplishments of the Hydrogen 101 project in South Carolina.
- Task 2. Hydrogen Education for Codes Officials
 - Subtask 1.1 - Assess, Design, Develop, Implement and Evaluate (Year 1)
 - The SCHFCA continues work with DOE and NREL to host a codes workshop in conjunction with the NHA conference in Columbia in March 2009.

Q2 2009

- Task 1. State and Local Government Officials Education
 - Subtask 1.1 - Assess, Design, Develop, Implement and Evaluate (Year 1)
 - The SCHFCA team conducted a working meeting in May to discuss next steps and action items. Work began on setting up sessions for the upcoming quarter and beyond. A presentation was given to the Upper Savannah Council of Governments. The audience was particularly interested in the environmental and human health impacts of the technology. The room was mostly community leaders (decision makers) that work on revitalization and low income housing issues. They are well-recognized in their communities and respected for their opinions and work.
 - Greenway Energy completed the draft of its curriculum report that outlines the teaching objectives for hydrogen and fuel cells as well as the training formats best suited to different

audiences. This assessment has been used in the creation of the presentations for different audiences and will continue to be revised based on feedback from presentations.

- Task 2. Hydrogen Education for Codes Officials
 - Subtask 1.1 - Assess, Design, Develop, Implement and Evaluate (Year 1)
 - The SCHFCA partnered with DOE/NREL to coordinate a Codes Officials Permitting Workshop conducted at the South Carolina Fire Academy in Columbia, SC on April 3, 2009. This provided several opportunities. First, it allowed the project team to interact and observe hydrogen codes experts deliver relevant materials to a segment of our target audience. Second, the event facilitated our objective of connecting our audience to relevant and up to date educational materials. The materials gathered at the event will be integrated into the curriculum already created by the SCHFCA team.

FY 2009 Publications/Presentations

1. Baxter-Clemmons, S., “Status of Hydrogen 101”, presentation to the Merit Review panel at the 2009 DOE Annual Merit Review, Crystal City Marriott, Washington, D.C., May 21, 2009.
2. Greenway, S., “Hydrogen 101: Education for State and Local Decision Makers”, presentation made to the Municipal Association of South Carolina, Columbia, SC, February 19, 2009.
3. Baxter-Clemmons S., Greenway, S., “Hydrogen 101: Education for State and Local Decision Makers”, webinar presented to officials attending the NHA Conference 2009, Online, March 24, 2009.
4. Baxter-Clemmons S., “Hydrogen 101: Education for State and Local Decision Makers”, presentation to the Upper Savannah Council of Governments, Myrtle Beach, SC, May 7, 2009.

Conclusions and Future Directions

The project is moving in the right direction and is on track. An increase in event frequency will begin in Q3 of 2009 with the addition of monthly webinars for an undetermined duration. The team plans to continue in-person events every 1-2 months. Three seminars and presentations are planned as of the final draft of this report, including one to the Waccamaw Council of Governments, Central Midlands Council of Governments and the South Carolina Rural Water Association. Many additional prospects are in development. The curriculum and materials will be updated as needed.

X.11 VA-MD-DC Hydrogen Education for Decision Makers

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Project Start Date: September 1, 2008

Project End Date: September 30, 2010

Objectives

The goal of the two-year project is to increase a targeted audience's understanding of hydrogen and fuel cells, including early market applications, and to provide specific examples of actions that the targeted audience – state and local government leaders – can take to support the development and use of hydrogen and fuel cell technology leading to better understanding of the community benefits that can result. The main objectives of the two-year project are to:

- Conduct a dozen in-person workshops by technical experts and professional educators.
- Produce video resources for public television, seminar use, and DOE/general public.
- Use hardware demonstrations when possible and provide real-world examples of technology.
- Produce electronic “magazine” articles on hydrogen technology demonstrations and other instructional project deliverables.

Technical Barriers

This project addresses the following technical barriers from the Education section (3.9) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) Lack of Readily Available, Objective, and Technically Accurate Information
- (B) Mixed Messages
- (C) Disconnect between Hydrogen Information and Dissemination Networks
- (D) Lack of Educated Trainers and Training Opportunities
- (E) Difficulty in Measuring Success

Contribution to Achievement of DOE Education Milestones

This project will contribute to achievement of the following DOE milestones from the Education section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- Milestone 17: Hold “Hydrogen 101” seminars. (4Q 2008 through 4Q, 2009)

Accomplishments

The following has been accomplished from September 2008 – July 2009 by Virginia Clean Cities and project partners:

- Conducted three “Hydrogen 101” seminars in Virginia and Maryland, four more scheduled.
- Finished shooting for and production of year one MotorWeek video “Hydrogen Update.”
- Rough draft production of three “magazine” articles.
- Finishing completion of brand new Web site and special hydrogen section.
- Produced two versions of seminar curriculum, one is more general and geared towards introductory information while the other is a bit more technical. Both have been well received.
- Held ride-n-drives of Equinox fuel cell electric vehicle at two seminars.
- Fostered communication with policy-makers, and hydrogen is now large component of the energy plan of the candidate for the new Virginia's Governor.

Introduction

In order to change the way we use energy and to realize the vision of the hydrogen economy, not only will research and development need to persist by engineers and scientists, but decision makers will need to make informed public policy decisions and continue to support research and development as well as deployment activities. This project aims to raise awareness of hydrogen and fuel cell technologies, provide examples of what state and local government can do, and show how decision makers can support the development and use of hydrogen and fuel cell technologies. Our goal is to reach, by project's end, at least 50% of our target market (decision-makers and staffers at State Energy Offices, Departments of Environmental Protection, Departments of Transportation, and local government agencies) through all activities (seminars, newsletter, Web site, videos, outreach, etc.) and 20% of the target market concentrating on decision-makers and their senior staff through seminar attendance in the Virginia, Maryland and D.C. markets.

The objectives of this project are to provide hydrogen and fuel cell technology learning opportunities through seminars, multi-media and video resources, technical support, and demonstrations to local and state government and decision makers in order to help state and local government leaders become familiar with hydrogen and how it fits in the portfolio of near-term and long-term energy choices, develop an accurate understanding of hydrogen safety, recognize opportunities, and understand their part in facilitating use of hydrogen and fuel cell technologies.

Approach

Our primary approach is to host in-person seminars for our target market, state and local governments, which can be more clearly defined using the sub-groups selected for the 2004 baseline survey. Three state sub-groups were selected including State Energy Offices, Departments of Environmental Protection, and Departments of Transportation. Two local subgroups were selected including city and county local government agencies. Some activities, such as newsletters, Web sites, outreach, and videos, target these five sub-groups in a general sense and include all executives and staffers. The Hydrogen 101 seminars target decision-makers and those who inform them (i.e. executive staff).

Messaging ties to the hydrogen knowledge survey, on which the subprogram objectives and targets are based. Under DOE guidance, existing hydrogen education sub-program resources and new contributions by team members are considered. Educational content focuses

primarily on a basic understanding of hydrogen properties and the energy security and environmental benefits of hydrogen and fuel cell technologies, but also focuses on more technical subjects related to fuel cells and other modes of hydrogen energy conversion. Special consideration has been given to “following the technology” and resources also concentrate on areas where hydrogen and fuel cells are publicly visible through demonstration projects or early niche market commercialization efforts, such as the Defense Distribution Depot Susquehanna, PA hydrogen fuel cell forklift project.

Key to state and local government representative education is a broad understanding of how hydrogen supports decision-making on current opportunities and laying the foundation for long-term change. Additionally, providing real-world examples and demonstrations has been a key component of each seminar when demonstrations have been available. Such demonstrations have been well received.

Results

The major achievements to date include designing curriculum for and hosting three successful, and highly received seminars, and completing a comprehensive shooting schedule and production of a seven-minute video for seminar use and broadcasting on the Public Broadcasting Service (PBS). Additionally, as part of the shooting for the video, Virginia Clean Cities interviewed individuals to gather information for three electronic technology demonstration articles, which are nearing completion.

Seminar Results

The curriculum prepared and presented by Dr. Catherine E. Grégoire Padró of Los Alamos National Laboratory at the September 17, 2008 and April 29, 2009 seminars covered the following content:

- Our current energy system.
- What is hydrogen?
- Why hydrogen?
- What is a fuel cell?
- Hydrogen production, storage, distribution, and use.
- Environmental, energy and economic implications.
- Safety.
- The future of hydrogen and fuel cells.

At the April 29, 2009 seminar, a pre- and post-workshop quiz was given by Dr. Padró. The survey consists of 11 questions that were taken directly from the original DOE survey, conducted in 2004 (see Table 1) [1]. The idea for choosing these questions was to maintain the standard set of questions to gauge learning and to compare to the 2004 baseline.

TABLE 1. Pre- and Post-Seminar Survey Results from April 29, 2009
Event held in Chesterfield County, VA and taught by Catherine E. Grégoire Padró.

Pre- and Post- Seminar Survey Question	# Responses	% Correct Before	% Correct After
1. Hydrogen Pipelines Exist Nationwide (false)	18	77.78%	88.89%
2. In a hydrogen economy, hydrogen replaces fossil fuels as the dominant form of energy (true)	18	72.22%	77.78%
3. Hydrogen gas is toxic (false)	18	50.00%	88.89%
4. Fuel cells produce electricity through hydrogen combustion (false)	18	50.00%	77.78%
5. Hydrogen is too dangerous for everyday use by the general public (false)	18	100.00%	100.00%
6. Hydrogen is lighter than air (true)	18	88.89%	94.44%
7. Hydrogen has a distinct odor (false)	18	88.89%	94.44%
8. In which state or condition can hydrogen be stored? (chemical compound and liquid)	18	61.11%	83.33%
9. When using pure hydrogen, fuel cell vehicles generate electricity, water, and what else? (heat)	18	66.67%	83.33%
10. Hydrogen can be produced using which of the following sources of energy? (natural gas, sunlight, organic matter)	18	66.67%	83.33%
11. Which of these represents a type of fuel cell? (PEM)	18	38.89%	83.33%

The curriculum presented by Dr. Gregory Jackson and Dr. Peter Sunderland at the June 5, 2009 seminar held at the University of Maryland, College Park, covered the following content:

- Overview and introduction to hydrogen and fuel cells.
- Energy today and the potential of hydrogen.
- Hydrogen safety.
- Hydrogen production, storage, distribution, and use.
- Fuel cells and other modes of H₂ energy conversion.
- Permitting process.
- Short-term prospects and long-term vision.
- Research in fuel cells and H₂ at Maryland.
- Lab tours, a showing of the MotorWeek video and a ride-n-drive were also included.

The curriculum was changed considerably for the June 5, 2009 seminar and did not specifically address the topics included in the 2004 baseline survey. Therefore,

a survey that focused more on qualitative information related to seminar effectiveness and participant reception was administered. The results of this survey are seen in Table 2. Note only ten remained at the end of seminar, although 19 originally were accounted for.

TABLE 2. Results of University of Maryland, June 5, 2009, Seminar Survey

i. Overview and Introduction to Hydrogen & Fuel Cells		
Very Useful	Useful	Not Useful
8	2	0
ii. Our Current Energy System and the Potential of Hydrogen		
Very Useful	Useful	Not Useful
6	4	0
iii. Lab Tours		
Very Useful	Useful	Not Useful
6	3	1
iv. Hydrogen Safety		
Very Useful	Useful	Not Useful
9	1	0
v. MotorWeek Video		
Very Useful	Useful	Not Useful
7	3	0
vi. Ride-N-Drive		
Very Useful	Useful	Not Useful
7	3	0
vii. Hydrogen Production, Storage, Distribution and Use		
Very Useful	Useful	Not Useful
7	3	0
viii. Fuel Cells and their Relationship to H₂		
Very Useful	Useful	Not Useful
5	5	0
ix. Permitting Process		
Very Useful	Useful	Not Useful
0	8	1
x. Short-Term Prospects and Long-term Vision		
Very Useful	Useful	Not Useful
4	6	0
xi. Research in Maryland and Other Institutions		
Very Useful	Useful	Not Useful
5	5	0
xii. Closing Open Discussion		
Very Useful	Useful	Not Useful
2	7	0

TABLE 2. Results of University of Maryland, June 5, 2009, Seminar Survey (Continued)

xiii. Overall Event		
Very Useful	Useful	Not Useful
6	4	0
Why did you attend today's seminar?		
<ul style="list-style-type: none"> • Learn about hydrogen as a motor fuel. • Our office is the state regulator of motor fuel. We wanted to learn about what the future may be for hydrogen. • To develop greater understanding about current and future developments in use of hydrogen fuel cells. • To learn more about the industry since I just started working in it. • Interest in fuel cell technology in relation to commercial use in the transportation sector. • To gain more information on hydrogen. • Listen to active professors, drive GM Equinox, see Ballard laboratory. • To see program, potential use in training. • To see if this technology can be applied in our business now or within next 2 years. 		
What was the most interesting part of today's seminar?		
<ul style="list-style-type: none"> • Vehicle ride-n-drive. • We started with no real knowledge of hydrogen fuel cells. I feel as though I have a fair understanding of how they work, what their limitations are today, and the challenges they face. • Lab on safety and combustion. • The lab tours and seeing the Equinox because it's one thing to hear about fuel cells but actually seeing them in person was so valuable. • Driving the fuel cell vehicle and visiting the research labs. • All. • The lab tours and the overviews from those very knowledgeable professors. • Permitting – as I have not seen any presentations on this. • Everything. • How hydrogen is produced, different types of fuel cells, safety considerations. 		
What did we NOT cover today that you desired? How can we improve?		
<ul style="list-style-type: none"> • It was would nice for the professor to have more time. • More on safety, website, supplemental information; need more time for safety. • Perhaps a little more on cost of operating on fossil fuel versus hydrogen. 		
Other comments?		
<ul style="list-style-type: none"> • From a regulatory standpoint, I would be interested as this becomes a more viable fuel in terms of fuel quality (consumer getting what they pay for) and the ability to retain a fair portion of the use to fund the transportation trust fund. • Great event for making industry contacts. • Excellent presentation of issues, problems and solutions regarding use of hydrogen fuel cells as energy source. • Technical presentation was excellent from Greg Jackson; better detail for different sectors and research. 		

MotorWeek "Hydrogen Update" Video

Virginia Clean Cities worked with MotorWeek over several months to shoot footage for the first year video. Footage included several hydrogen dispensing stations on the east coast, many of current original equipment

manufacturer hydrogen fuel cell electric vehicles, and several early market hydrogen fuel cell pilot projects.

The video runs seven minutes and twenty seconds, and covers an introduction to hydrogen fuel cells as they relate to transportation and current research, development, and early market deployment activities.

The video was completed on June 1, 2009 and was shown at the June 5, 2009 seminar. The video will be cut to a few minutes and aired on MotorWeek in August 2009. MotorWeek is available on PBS and the SPEED channel. The video is also available for viewing on the Virginia Clean Cities Web site at www.hrcc.org.

Conclusions and Future Directions

The seminars that have been held to date have been very well received and the participants' knowledge of hydrogen and fuel cell technology has increased as indicated by the surveys. The next year of this project will focus on the following outputs described below, as well as continuous improvement.

Future Project Outputs

Over the next year, Virginia Clean Cities and partners will:

- Host an additional seven to nine in-person seminars and Webinars will be held in Virginia, Maryland and D.C. and work with the National Energy Education Development Project to co-host teacher training seminars.
- Complete eight "technology profiles"/case studies. The first three that are under development include: University of Maryland and Ballard Power Systems research and development, South Carolina's hydrogen and fuel cell work, and the Defense Depot Susquehanna Pennsylvania fuel cell forklift demonstration.
- Finish shooting and produce a second MotorWeek video.
- Conduct follow-up surveys of participants from past seminars.
- Record and pod-cast several of the seminars to be linked from the Web site.
- Finish completion on new interactive Web site to include all content produced from project and other resources from education awards.
- Attend events to discuss and promote project and project outputs.

Planning and Improvements

A meeting between the past instructors and other key stakeholders will be held during the second week of November 2009 to discuss blending the two sets of

curricula developed, and other key project components. DOE project managers will be included in the discussion to ensure future curriculum improvement includes current and key DOE messaging.

Key partnerships have been developed over the last year with organizations such as the Local Governments for Sustainability, the National Association of Counties, the Virginia Association of Counties, the Virginia Municipal League, and climate communities. Virginia Clean Cities is working with these partners to host upcoming events specifically targeting their members, who represent the target audience for this project. This will also aide in increasing participation at the events. Due to extreme travel restrictions, attendance has been lower than hoped for at the past two seminars.

A discussion about extracting the key information from curricula will take place at the project development meeting in order to determine an agenda for the Webinar series. Webinars will begin in early 2010 in order to increase audience reach and allow for travel-restricted audience to attend.

Surveys for future seminars will include both qualitative and quantitative metrics to gauge participating learning, as well as reception and seminar deficiencies.

Key Issues

The main issues relate to Virginia Clean Cities undergoing some major organizational and staff changes, as well as the Recovery Act placing extra demands on current staff and requiring a shifting of focus to respond to extremely tight timelines. The project manager for the day-to-day management of this project transitioned to a new position and Virginia Clean Cities has been working to fast-track reorganization and the hiring of a new project manager. The position will be filled by early September 2009.

FY 2009 Publications/Presentations

1. Catherine Padro PowerPoint for 9/17/2008 seminar.
2. Al Christopher PowerPoint for 9/17/2008 seminar.
3. Catherine Padro PowerPoint for 4/29/09 seminar.
4. Chelsea Jenkins PowerPoint for 4/29/09 seminar.
5. Dr. Gregory Jackson PowerPoint for 6/5 seminar.
6. Dr. Peter Sunderland PowerPoint for 6/5 seminar.

All presentations available at <http://www.hrccc.org/hydrogen/hydrogenseminars.html>.

References

1. Hydrogen Knowledge and Opinions Survey, 2004. "Results: State and Local Government Survey" pps. 47-65. Available online at http://www1.eere.energy.gov/hydrogenandfuelcells/pdfs/survey_main_report.pdf.

X.12 State and Local Partnership Building

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Contract Number: DE-FC36-08GO18116

Project Start Date: September 1, 2008

Project End Date: August 30, 2010

Objectives

- Foster strong relationships among federal, state, and local government officials, industry, and appropriate stakeholders.
- Serve as a conduit between the DOE and state and local government decision makers.
- Provide technically accurate and objective information to government decision-makers and identified stakeholders to improve/enhance decision making.
- Increase the knowledge base and improve awareness regarding the use of hydrogen and fuel cells.
- Provide support for hydrogen and fuel cells in early market applications, consistent with DOE's market transformation efforts.

Technical Barriers

This project addresses the following technical barriers from the Education section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) Lack of Readily Available, Objective, and Technically Accurate Information
- (B) Mixed Messages
- (C) Disconnect Between Hydrogen Information and Dissemination Networks

- (D) Lack of Educated Trainers and Training Opportunities
- (F) Difficulty of Measuring Success

This project will contribute to achievement of the following DOE milestones from the Education section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- **Milestone 17:** Hold "Hydrogen 101" seminars. (4Q, 2008 through 4Q, 2012)
- **Milestone 29:** Evaluate knowledge and opinion of hydrogen technology of key target audit audiences and progress toward meeting objectives. (4Q, 2009)
- **Milestone 30:** Evaluate knowledge and opinion of hydrogen technology of key target audit audiences and progress toward meeting objectives. (4Q, 2012)

Accomplishments

- Identified key stakeholders at the local and state level to expand and strengthen partnerships.
- Performed a preliminary survey of local stakeholders and decision makers.
- Developed resources to analyze potential sites for hydrogen and fuel cell development. Resources include a database of potential sites for technology deployment and a report to detail criteria for the deployment of technologies for transportation, stationary, and portable applications.
- Developed a Web-based virtual regional resource center that provides online information, models and other tools to assist local, state and regional planners quantify the costs and benefits of hydrogen and fuel cell technology at potential sites. Models address environmental value, energy management, renewable hydrogen generation, distributed technology comparisons, and cost/economics of stationary fuel cells.
- Began planning a workshop for outreach to local stakeholders and decision makers.

Introduction

This project assists with the building of partnerships between the DOE, states and municipalities. The Connecticut Center for Advanced Technology, Inc. (CCAT) is implementing a process and structure that provides an opportunity for federal, regional, state, and local involvement to encourage and promote the use

of hydrogen and fuel cell technology. The structure includes leadership by the DOE; the establishment of collaborative meetings, workshops, and briefings to provide information to municipal and state decision makers; the provision of assistance to municipalities for the development of local energy plans; support for state stakeholder groups to implement initiatives in support of state and federal policies; and implementation of strategies to facilitate the deployment of hydrogen and fuel cell systems in the state.

CCAT developed a virtual regional resource center (RRC) that provides online information, models, and other tools to assist decision makers and end users to quantify the costs and benefits of hydrogen and fuel cell technology at potential sites. The RRC will assist local and state planners and decision-makers in identifying potential opportunities. CCAT developed models that assess environmental value, energy management, renewable energy, cost and economics, and comparisons of competing technologies.

Approach

CCAT's approach is to develop resources for hydrogen and fuel cell deployment to aid in the education of state and local decision makers. These resources include online information, models, and tools for potential users to analyze the costs and benefits of hydrogen and fuel cell technology. Coordination and cooperation is sought by both local and state decision-makers in order to introduce hydrogen and fuel cell technology in early market applications. The project uses local "bottoms up" decisions guided by state/regional "tops down" assistance to help reduce conflict, improve state/regional and municipal relations, and provide better solutions to community-based energy problems. Because of the high risk and high capital cost of implementing new technologies, CCAT will also coordinate with local, state, and regional decision makers to identify innovative funding and procurement mechanisms, such as group purchases and corporate tax credits, to encourage market growth, reduce costs, and increase public acceptance.

Results

The major achievement of the project to date was the development of models that assess environmental value, energy management, renewable energy, cost and economics, and comparisons of competing technologies. These models make available information for non-technical and technical audiences, including state and local decision makers and potential end users and will be an integral component of education and outreach efforts. The models are currently under review by the DOE and are described in the following.

Environmental Model

The Environmental Model assesses the environmental benefits of hydrogen and fuel cell applications compared with other conventional technologies. The model can be used to assess potential emissions reductions, including greenhouse gases, using hydrogen and fuel cell technology.

Economic/Cost Model

The Economic/Cost Model assesses potential yearly heating and electricity cost savings when using a commercially available fuel cell for baseload power. The model allows users to assess the economic viability of a fuel cell system.

Energy Management Model

The Energy Management Model assesses the efficiency benefits of stationary fuel cell applications. The model can be used to assess the potential energy savings using a fuel cell to replace conventional electricity generating technologies.

Distributed Technology Comparison

The Distributed Technology Comparison allows a user to compare fuel cells with other distributed energy technologies including microturbines, combustion turbines, reciprocating engines, photovoltaic systems, and wind turbines, based on certain criteria such as installation cost, efficiency, emissions, heat rate, etc .

Hydrogen Generation from Renewable Technology Model

The Renewables to Hydrogen Model assesses wind, photovoltaic and hydroelectric power generation technologies to identify hydrogen production capacities and average cost per kilogram of generated hydrogen from these renewable technologies.

CCAT has also assessed the level of knowledge and opinions of hydrogen and fuel cell technologies of local and state stakeholders to determine the effectiveness of the project implementation. In addition, other tools have been developed including criteria for the deployment of hydrogen and fuel cell technologies and educational videos that will serve to increase the awareness levels of local and state stakeholders.

Conclusions and Future Directions

This partnership effort has successfully created models and tools that will allow for effective deployment of hydrogen and fuel cell technologies in early market applications. Models and tools have been created to facilitate the education of decision makers and end

users as well as the ability to analyze potential sites for hydrogen and fuel cell technology.

Next steps include providing instruction to local and state decision makers on the use of models and tools within the RRC and information on market awareness, regulatory issues, safety, and local energy planning to increase early market applications. CCAT will facilitate the dissemination of information to municipal decision makers and stakeholders, and keep state officials abreast of activities to deploy hydrogen and fuel cell technologies through the use of collaborative meetings and briefings to achieve state goals including energy reliability, security, efficiency, emissions and economic development. CCAT will also provide the information on financial and investment opportunities to encourage market growth, reduce costs, and increase public acceptance.

FY 2009 Publications/Presentations

1. Rinebold, J.M., “2009 DOE Hydrogen Program Review Presentation”, presentation at the 2009 DOE Annual Merit Review and Peer Evaluation Meeting, Arlington, Virginia, May 21, 2009.

X.13 Raising H₂ and Fuel Cell Awareness in Ohio*

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Contract Number: DE-FG36-08GO18117

Subcontractor:
Edison Material Technology Center, Dayton, OH

Project Start Date: March 2009
Project End Date: August 31, 2010

*Congressionally directed project

Contribution to Achievement of DOE Education Milestones

This project will contribute of the following DOE Milestones from the Education section of the Hydrogen Fuel Cells and Infrastructure Technologies Program Multiyear Research Development and Demonstration Plan:

- **Milestone 11:** Develop set of introductory materials suitable for a non technical audience (3Q, 2009)
- **Milestone 13:** Develop material for community seminars (3Q, 2009)
- **Milestone 16:** Develop database of state activities (3Q, 2009)
- **Milestone 17:** Hold "Hydrogen 101" seminars (3Q, 2009 through 3Q, 2010)

Accomplishments

- On May 27 and 28, over 250 people attended the 2009 Ohio Fuel Cell Symposium at Kent State Stark Branch, North Canton, Ohio.
- On May 27, two fuel cell community leaders' forums were educated on fuel cells and the hydrogen economy. Over 100 people attended these two events.
- On May 28 the audience was educated on fuel cells as they relate to power generation solutions for the grid and additionally on fuel cells in the market today.

Objectives

- Increase understanding of hydrogen and fuel cell technologies among state and local governments by 10 percent compared to 2004 baseline.
- Increase knowledge of hydrogen and fuel cell technologies among key target populations (state and local governments) by 20 percent compared to 2004 baseline.

Technical Barriers

This project addresses the following technical barriers from the education section of the Hydrogen, Fuel Cells and Infrastructure Technology Program Multiyear Research Development and Demonstration Plan:

- (A) Lack of Readily Available, Objective, and Technically Accurate Information
- (B) Mixed Messages
- (C) Disconnect Between Hydrogen Information and Dissemination Networks
- (D) Lack of Educated Trainers and Training Opportunities
- (E) Regional Differences
- (F) Difficulty of Measuring Success

Introduction

The Ohio Fuel Cell Coalition was tasked with raising the awareness and understanding of fuel cells and the hydrogen economy. In 2009 through 2010 the Ohio Fuel Cell Coalition will hold ten community leaders forums. A community leader's forum was held in conjunction with the 2009 Ohio Fuel Cell Symposium. On May 27 and 28 hundreds of people gathered at Kent State Stark for the 2009 Ohio Fuel Cell Symposium. The symposium presented by the Ohio Fuel Cells Coalition began with two DOE Community Leader forums where participants had an opportunity to learn about fuel cells and the hydrogen economy. Day two of the symposium opened with the focus on the theme of fuel cells as it relates to power generation solutions for the grid. Lionel Batty, chairman of the board of directors for the Ohio Fuel Cell Coalition kicked off the day with opening remarks followed by the morning

featured speakers, which included Elizabeth Shaw of First Energy Corp., Ethan Brown of Ballard Power System, John M. Schneider of American Power, and Mark Fleiner of Rolls-Royce Fuel Cell (U.S.) Inc.

The 2009 Ohio Fuel Cell Symposium drew over 250 people from around the State of Ohio and across the country. Additionally attendees had an opportunity to interact with and visit the booths of more than 35 exhibitors, which included companies from fuel cell integrators, to manufacturers, to component suppliers and research entities. **This event allowed the Ohio Fuel Cell Coalition to educate over 350 individuals on fuel cells and the hydrogen economy thus more than exceeding our expectations.**

Approach

The approach we used and will be using for the ten Community Leaders Forums will be presentations by the Ohio Fuel Cell Coalition in conjunction with regional leaders. The presentations will be followed by question and answer periods followed up by informal discussions on fuel cells and the hydrogen economy.

Results

The results have been spelled out in greater detail above, but in summary the one activity we did hold was very successful as 350 people attended. We followed this activity with a survey and the survey results were very positive in that the participants had a significant increase in knowledge and awareness of fuel cells and the hydrogen economy.

Conclusions and Future Directions

We have received input on the first Community Leaders Forum and that input will be incorporated in future events. The following Community Leaders Forums will be held in the next 6 weeks:

- August 21, 2009 - ADA/Lima/Ohio Northern University Community Leaders Forum
- September 2, 2009 – Youngstown State University, Youngstown, Ohio
- September 14, 2009 – Dayton, Ohio
- September 28, 2009 – Columbus, Ohio

X.14 H2 and You: A Public Education Initiative by the Hydrogen Education Foundation

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Contract Number: Contractor did not supply

Project Start Date: April 1, 2009
Project End Date: Sept 30, 2009

Contribution to Achievement of DOE Education Milestones

This project will contribute to achievement of the following DOE milestones from the Education section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- **Milestone 11:** Develop set of introductory materials suitable for a non-technical audience. (4Q, 2006)
- **Milestone 13:** Develop materials for community seminars. (4Q, 2008)
- **Milestone 14:** Hold community seminars to introduce local residents to hydrogen. (4Q, 2008 through 4Q, 2012)
- **Milestone 17:** Hold “Hydrogen 101” seminars. (4Q, 2008 through 4Q, 2012)
- **Milestone 29:** Evaluate knowledge and opinion of hydrogen technology of key target audiences and progress toward meeting objectives. (4Q, 2009)

Objectives

- Increase awareness and understanding of hydrogen and hydrogen-fueled technologies among the general public.
- Educate leading hydrogen influencers to validate hydrogen’s impact and potential.
- Establish hydrogen as an essential part of the long-term energy mix.
- Capitalize on related initiatives and resources from program steering committee partners.

Technical Barriers

This project addresses the following technical barriers from the Education section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) Lack of Readily Available, Objective, and Technically Accurate Information
- (B) Mixed Messages
- (C) Disconnect Between Hydrogen Information and Dissemination Networks
- (E) Regional Differences
- (F) Difficulty of Measuring Success

Accomplishments

- Increased visits to the H2 and You Web site to an average of 4,300+ visits per month.
- Expanded to Social Networking sites Twitter, Facebook, and LinkedIn to increase audience for public education. All are experienced average to significant growth in audience size and interaction with target audiences since launch.
- Created online networks that allow the HEF to “train the trainer.” Through the social networks, other experts and new enthusiasts, like Project Driveway drivers, have a forum to interact equally with experts and the less informed to share learnings, news, pictures, video and other information. www.H2andyou.org
- Created the H2 and You photo contest with online voting and donated prizes from companies in the industry. Vote for your favorite today at <http://www.h2andyou.org/photoContest.asp>
- Continued execution of program activities:
 - Stage is set for continued visibility for H2 and You.
- Conducted multiple one-on-one interviews with major publications (e.g. New York Times, Wall Street Journal, USA Today, Associated Press, etc.).
- Participation as MC and spokesperson for the hydrogen industry during the first four days of the

Hydrogen Road Tour 2009, which attracted 53.5 million online impressions.

- Responded to online news regularly to provide accurate hydrogen facts to meet the DOE milestone of public education.
- Responded promptly to inaccurate information: in online forums when the public was misinformed and 1-on-1 when a reporter was misinformed with requests for a correction.
- Additional oversight provided by industry and government representatives through the H2 and You Steering Committee.
- Additional funds contributed by Daimler, Shell Hydrogen, Linde, Hydrogen Utility Group, Nebraska Public Power, Xcel Energy and Proton Energy Systems.

Introduction

H2 and You is a project of the Hydrogen Education Foundation, a 501(c)(3) organization, dedicated to increasing understanding about hydrogen. It has been designed to take the complexity, confusion and intimidating science out of hydrogen. H2 and You is making it easy to understand what hydrogen is, how it applies to people's daily lives, and how it fits into the alternative energy picture. The project's focus for 2009 has been on increasing interactivity, so people can easily learn more about hydrogen and fuel cells, take action to show their support, and actively share what they have learned with others. This has created an environment for multiple "train-the-trainer" interactions every day.

Approach

To reach the most people possible, a strategic, targeted approach has been developed. Outreach materials have been developed to be understood by the general public but distributed through three main channels:

- Key media.
- A network of about 250 industry eminents including a variety of leaders across different industries.
- Online engagement/Web 2.0.

Results

A major achievement for H2 and You in 2009 was the expansion of online engagement to social networking. The H2 and You program now utilizes Facebook, Twitter, and LinkedIn in addition to the popular H2 and You site to disseminate hydrogen education to large audiences. The goal of using these

tools is to educate the general public, gain awareness and understanding about hydrogen, and provide those with an interest in hydrogen a place to interact and get involved with spreading accurate information about hydrogen and fuel cells. The H2 and You program had much success in the growth of these networks in 2009 (Figure 1).

To maintain positive media relations, the H2 and You staff conducted multiple one-on-one interviews with key media. Some of the media interviews conducted were for the New York Times, the Wall Street Journal, USA Today, and the Associated Press, among others. Being consistent with the H2 and You goal of education, these interviews were conducted to ensure positive and accurate reporting on hydrogen. Where inaccuracies were discovered as a result of these or other pieces, reporters were promptly contacted to make corrections. The H2 and You program promoted and participated in the Hydrogen Road Tour 2009, which attracted 53.5 million online impressions.

H2 and You tracked interactions with influencers based on news and other commentary. The H2 and You staff responded rapidly in the blogosphere to augment support or correct inaccuracies or misperceptions, thus educating the public on hydrogen energy. The "blogs" and responses were presented to the steering committee monthly. Some blogs H2 and You responded to included Green Car Congress, Autoblog Green, NY Times blog, and multiple postings on the Hydrogen Road Tour blog. In tracking these blogs and news, the H2 and You program has concluded the tone about hydrogen is noticeably improving and HEF is observing a growing number of news articles on hydrogen and fuel cells (Figure 2) with a mostly neutral tone.

FIGURE 1. Growth of H2 and You Social Networks by Week May-Sept 2009

FIGURE 2. Tone of Hydrogen Articles and Blogs by Month in 2009

FIGURE 3. H2 and You Web Site Visits by Month in Fiscal Year 2009

The H2 and You Web site (www.h2andyou.com) is an information source and now a center for interaction for target audiences and the general public to gain understanding of hydrogen without needing to sift through technical language. Figure 3 shows the number of visits to the site each month. In 2009, there were 4,300+ visits every month. This is an increase from the previous year. There were 160 sites referring visitors to the H2 and You site.

Conclusions and Future Directions

Summary

- Cost-effective project for educating the public about hydrogen (2 DOE \$ = 5 Project \$), thanks to additional support from Daimler, Shell Hydrogen, Linde, Hydrogen Utility Group, Nebraska Public Power, Xcel Energy and Proton Energy Systems.
- The multi-tiered approach across media, blogs and other influencers is having an impact.
- Directly addresses Education Multi-Year Research, Development and Demonstration Plan barriers.
- Solid foundation in place and measurable progress is beginning.

- Clear path spelled out for continuation of work and potential expansion.
- Expansion to Social Networking sites Twitter, Facebook, and LinkedIn proved to expand H2 and You's reach exponentially and provided several more opportunities a day for interaction on hydrogen and fuel cell education.
- Monthly reports to the DOE and other organizations on the H2 and You Steering Committee has guided project.

Future Work

- Deepen and broaden existing educational activities:
 - Showcase hydrogen-focused developments in national media and most popular energy and environmental blogs.
 - Daily content delivered to encourage interaction through social networks.
 - Integration, synergies and regular communication with DOE and other organizations on steering committee.
 - Finish conversion of H2 and You Web site from purely informational to information and action, thus being the location for hydrogen supporters to act and support hydrogen initiatives.
- Build a groundswell of consumer support:
 - Continue with existing approach to consumer education.
 - Continue to expand focus and implement tactics to support:
 - Consumer advocacy
 - Viral marketing
 - DOE remains a resource for information and assistance.

X.15 Hydrogen Education State Partnership Project

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Contract Number: DE-FG36-08GO18111

Subcontractor:
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Project Start Date: October 1, 2008
Project End Date: September 30, 2011

- (D) Lack of Educated Trainers and Training Opportunities
- (E) Regional Differences
- (F) Difficulty of Measuring Success

Contribution to Achievement of DOE Education Milestones

This project will contribute to achievement of the following DOE milestones from the Education section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- **Milestone 16:** Develop database of state activities. (2Q, 2007). This project will be documenting state policies, programs and other state activities which are supporting hydrogen and fuel cell investments, industries and applications.

Accomplishments

- Developed network and listserve of state legislators and clean energy officials interested in hydrogen and fuel cell policies.
- Completed drafts of papers on hydrogen technology basics and state policy best practices.

Objectives

- Provide information and technical assistance to state policy leaders and state renewable energy programs in the development of effective hydrogen fuel cell programs.
- Identify and foster hydrogen program best practices.
- Identify and promote strategic opportunities for states and the Department of Energy (DOE) to advance hydrogen technology deployment through partnerships, collaboration, and targeted activities.

Technical Barriers

This project addresses the following technical barriers from the Education section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) Lack of Readily Available, Objective, and Technically Accurate Information
- (B) Mixed Messages
- (C) Disconnect Between Hydrogen Information and Dissemination Networks

Introduction

State policies can represent both significant barriers and a supportive framework to encouraging the development of hydrogen infrastructure and the adoption of hydrogen and fuel cell technologies for stationary and other non-transportation applications. Some of these policies are analogous to those for other distributed energy technologies (e.g., utility regulations governing interconnection); others are unique to hydrogen (e.g., policies governing hydrogen transportation and dispensing). In addition, the support of state clean energy funds for hydrogen and fuel cell demonstration projects can play an important role in raising the visibility and market interest in these technologies. Finally, coordinated state efforts, as evidenced by several of the state hydrogen collaboratives, can drive the development of hydrogen industry clusters.

In this project, CESA will track, identify, evaluate, communicate, and facilitate state adoption of effective financial, policy, and technology activities and best

practices that accelerate fuel cell and hydrogen technologies. CESA will use its membership network to effectively educate state clean energy policy makers, program managers, and decision makers about fuel cell and hydrogen technologies and the efforts by states to advance these technologies. With the assistance of the National Council of State Legislators (NCSL), CESA will have access to an effective forum for outreach and communication with state legislators from all 50 states on hydrogen issues and policies.

Approach

There are several major steps in the project.

- **Identification and Promotion of Best Practices:** CESA and its sub-contractor are assessing existing state hydrogen and fuel cell programs to identify and promote best practices and to develop case studies of exemplary programs.
- **Targeted Outreach:** Utilizing this initial work, CESA will provide state clean energy fund managers and state legislatures (through the NCSL) information and targeted outreach materials to educate them on the merits, opportunities, policies and programs proven effective for advancing fuel cell and hydrogen deployment. This information will also include a primer on fuel cell technologies including applications for back-up power in critical facilities.
- **Communications:** CESA is using its existing clean energy fund network as well as a listserve and bi-monthly conference calls to provide current information on hydrogen and fuel cell activities, trends, program elements and policies in different states.
- **Coordination:** CESA is coordinating communication among other DOE hydrogen education grantees to ensure that projects are coordinated and resources, programs and lessons learned from grantees and their states can be shared among the network of other education and outreach grantees.

Results

State Fuel Cell and Hydrogen Programs Survey and Recommendations Report

CESA completed a survey of its members on their hydrogen and fuel cell support and policies in their states. CESA also surveyed a wider listserve made up of members of the bi-monthly DOE/National Hydrogen Association (NHA)/CESA state hydrogen calls. This group includes non-profits, policy makers and advocacy groups in most of the 50 states.

Based on these surveys and further research, CESA's subcontractor, Dr. Timothy Lipman, has

completed an initial draft of a paper surveying and providing recommendations for best state policies to support hydrogen infrastructure and stationary fuel cell applications. This report will cover the benefits and incentives to states of supporting hydrogen and fuel cell technologies through public policies and financial incentives. The report will review in depth the leading state policies with an analysis of impacts. Given these results, as well as lessons learned from other clean energy technology policy support, the report provides recommendations to states on how to best promote hydrogen in their state and how to best direct limited public finance to advance the industry in their state. The report will be completed August 2009.

The report focuses on noteworthy hydrogen and fuel cell state/regional efforts in the following states with an emphasis on stationary programs and will include efforts both for commercialization as well as research, development and manufacturing:

- California - self-generation incentive program and CASFCC
- Connecticut - Connecticut Hydrogen-Fuel Cell Coalition
- Michigan - NextEnergy
- Texas - Fuel Cells Texas
- South Carolina Hydrogen and Fuel Cell Alliance
- Florida Hydrogen Initiative
- Ohio Fuel Cell Corridor
- Hawaii
- Illinois

Case Studies

Based on this research, CESA will identify two to three case studies to be completed by early 2010, with an additional two to three case studies to be completed in the following year. We have identified an initial state, Hawaii, to build a case study around. Hawaii has a well-coordinated, well-funded hydrogen energy development program with a number of high-visibility fuel cell applications as well as innovative policies including a \$10 million public venture capital and cost-sharing fund. In July CESA did a site visit to Hawaii's fuel cell test facility and to meet with University of Hawaii researchers and staff from Hawaii's state energy office to learn more about the history, impacts and future plans of the project.

Technology Assessment

CESA's sub-contractor, Dr. Timothy Lipman, has written a draft of his Fuel Cell Technologies Technical Overview paper. This paper covers the advantages of different fuel cell technologies, current economics, and best applications for stationary fuel cells in distributed

generation, back-up and critical power applications. The goal of this report is to help policy makers understand that hydrogen and fuel cells are technologies of today and to direct policies and incentives towards the most promising technologies and applications as well as significant barriers. The report will be completed in August 2009. Topics covered include: commercialization status.

- Performance and economic issues.
- Technology and system industry trends.
- Remaining hurdles and obstacles (cost issues, varying DG policies, etc.).
- Assessment of potential greenhouse gas savings from stationary fuel cells.
- Attractive niche fuel cell markets, e.g. premium power, emergency backup, etc.
- How fuel cells/hydrogen fit into an overall state energy portfolio.
- How fuel cell and hydrogen markets are likely to evolve over the short/medium/long term.
- Interplay between stationary and transportation hydrogen markets.

Bi-Monthly Conference Calls with DOE and NHA on Fuels Cells and Hydrogen Education

CESA, through Clean Energy Group, works with DOE and NHA to co-host bi-monthly conference calls on state and regional hydrogen fuel cell initiatives. These informational calls cover various topics to assist state and regional hydrogen initiative leaders to share lessons learned, and discuss useful information about fuel cell and hydrogen projects and reports. CESA is working with DOE and NHA to expand call audiences.

Calls during this year included:

- September 10, 2008 – The California Fuel Cell Partnership's recently released "Vision for Transition to Fuel Cell Vehicle Commercialization" – highlights and key messages.
- December 17, 2008 – Hydrogen and fuel cell tax incentives – available and pending.
- February 4, 2009 – Fuel cell policy plan – the U.S. Fuel Cell Council has prepared a six-point plan to advance fuel cell research and commercialization over the next five years.
- March 30, 2009 – During the NHA annual conference in March, CESA was a co-sponsor of the State/Regional Hydrogen and Fuel Cells Initiative workshop along with NHA and the Department of Energy. This session, attended by 60 people, was an opportunity to learn about a variety of fuel cell applications and policies. Topics and speakers included the following:

- Hydrogen and Fuel Cell Tax Credits: An Overview. Ethan Brown, Director, Business Development, Ballard Power Systems.
- Telecom Backup Power: The business and regulatory case. Kevin Harris, Business Development & Sales Director, Hydrogenics Corporation.
- H2 Vehicles: Fuel Cell Vehicles vs. Battery Electric Vehicles. Sandy Thomas, President, H2Gen Innovations, Inc.
- Forklifts/Materials Handling: The business case. Warren Brower, Product Marketing Manager, GenDrive, Plug Power Inc.
- Infrastructure for Emerging Markets. Mike Ciotti, Project Manager – Hydrogen Solutions, The Linde Group and Tom Joseph, Business Development Manager, Air Products and Chemicals, Inc.
- Job Creation/Analysis in the Hydrogen/Fuel Cell Industry. Paul Aresta, Energy Information Manager, Connecticut Center for Advanced Technology.
- Combined Heat, Hydrogen and Power. Darlene Steward, National Renewable Energy Laboratory.

- June 11, 2009 – The call featured a review of the Department of Energy's current hydrogen and fuel cell program and funding priorities. The call also covered a summary of the NHA's 2009 "Hydrogen Road Show."

CESA is planning a joint hydrogen states call with CESA's regular monthly calls in order to engage more CESA fund managers. The call topic is planned to cover Hawaii's "Renewables to Hydrogen" fund.

Steering Committee

CESA has begun to host bi-monthly calls with other DOE Hydrogen Education Topic 1 award recipients to share program successes and state policies in advancing hydrogen and fuel cells. Relevant information and policy developments are also being posted on the hydrogen collaborative listserv that CESA has initiated.

Outreach and Communications

To help with the communication, education, and network development components of this project, CESA is maintaining a fuel cell and hydrogen Web page and listserv for CESA members and other state leaders identified during this project. The Web page (<http://www.cleanenergystates.org/JointProjects/hydrogen.html>) provides current information on state hydrogen and fuel cell activities, trends, program elements, etc. The listserv will help CESA effectively communicate

state progress on hydrogen issues, identify high-priority opportunities for action, and share this information with its network of CESA members, NCSL members, and other interested parties.

Conclusions and Future Directions

Conclusions

- **State Policies and Incentives Matter:** Our survey and research have shown that states which have adopted proactive policy and financial incentives to support hydrogen and fuel cells in their states have seen significant industry growth and increased number of stationary installations.
- **Niche Markets will Advance the Industry:** Currently, the most promising areas for fuel cell growth appear to be in niche markets, particularly materials handling and critical/backup power. Applications in these areas are growing and are commercially competitive. As these applications grow, states can expect that other stationary and niche markets will also benefit. Given these developments, we will recommend that states focus in the near term on facilitating and promoting these applications while also looking to regulations, codes and standards that can promote other stationary applications in the midterm.

Future Directions

- **State Policy Recommendations:** Research will be completed on state policies and recommendations. This research will be updated next year as more states adopt supportive policies.
- **Communications and Outreach:**
 - **NCSL:** During the coming year, CESA will be working with NCSL. We will present the results of our research and recommendations during two conference meetings of NCSL. We will also communicate the results in a magazine article and a short briefing paper which NCSL sends to its members monthly.
 - **Other Forums:** We will be looking for opportunities to present in other forums, including NHA's annual conference in May 2010 and CESA bi-annual meetings.
 - **Bi-monthly Calls and Electronic Communications:** We will continue to work with DOE and NHA to lead the bi-monthly state hydrogen calls and continue to manage and grow our Web page and listserve. We will use the listserve to disseminate report results as well as to request feedback and updates on the results of our research and policy recommendations.

X.16 Hydrogen Technology and Energy Curriculum (HyTEC)

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Contract Number: DE-FG36-04-GO14277

Subcontractor:

Schatz Energy Research Center,
Humboldt State University, Arcata, CA

Project Start Date: September 1, 2004

Project End Date: February 28, 2012

Objectives

- Develop, field test, revise, publish, and disseminate three curriculum modules and integrate hydrogen and fuel cells into existing LHS high school materials.
- Develop and implement a professional development plan for teachers who will use the materials.
- Develop a model for collaboration among school districts, informal science centers, university scientists, local transportation agencies, and other leaders in the field.
- Disseminate the materials to a broad national audience.
- Evaluate the quality and effectiveness of the curriculum materials and professional development strategies.

Technical Barriers

This project addresses the following technical barriers from the Education section (3.9.5) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) Lack of Readily Available, Objective, and Technically Accurate Information
- (C) Disconnect between Hydrogen Information and Dissemination Networks
- (D) Lack of Educated Trainers and Training Opportunities
- (E) Regional Differences
- (F) Difficulty of Measuring Success

Contribution to Achievement of DOE Education Milestones

This project will contribute to achievement of the following DOE milestones from the Education section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- **Milestone 26:** Develop modules for high schools. (4Q, 2007))
- **Milestone 27:** Launch high school teacher professional development. (4Q, 2008 through 3Q, 2011)

Accomplishments

- The complete curriculum module was nationally field tested during the 2008–2009 school year by 13 teachers in diverse public, parochial, and alternative high schools in the San Francisco East Bay, California; Bellevue, Washington; and Dublin, Ohio. Input from these classrooms led to additional revisions in June 2009.
- A three-day professional development workshop was delivered to a total of 19 high school teachers in June 2009. The workshop was held at Lawrence Berkeley National Laboratory, in collaboration with their Center for Science and Engineering Education.
- Four presentations were made to secondary science educators and hydrogen and fuel cell professionals.
- The project entered into a contractual agreement with Lab-Aids, Inc., which has produced prototype kit components for testing and will commercialize the print and kit materials.

Introduction

This project is producing a curriculum module about hydrogen and fuel cells for high school students. A group of experienced science curriculum developers,

teacher professional developers, leaders in the field of hydrogen and fuel cell technology and its application to transportation, and the publishers of instructional materials are collaborating to develop commercial educational modules that will fit into high school courses such as physical science, chemistry, environmental science, and physics. In order to ensure that it will fit into typical high school classrooms, the module addresses topics teachers usually teach and correlates to the National Science Education Standards and/or state and local standards. This project is also developing professional development workshops to prepare teachers to teach the curriculum and develop teacher leaders. Project evaluation focuses on investigating students' progress toward the intended learning goals and evaluating the professional development workshops.

In the past year, a limited national field test was held in three sites in order to test the materials in a variety of locations and classroom settings. Teachers provided extensive feedback that has been used to fine-tune the curriculum and prepare for commercialization of the print and kit materials and revise the project website and Web-based simulation. In addition, 19 teachers received three days of professional development in order to prepare them to teach the curriculum in the coming school year.

Approach

The curriculum materials are developed and revised through a close collaboration between curriculum developers at the LHS, scientists and engineers at the Schatz Energy Research Center (SERC), experienced teacher associates, local and national field test teachers, and Lab-Aids, Inc., an established publisher of kit-based science curriculum materials. The materials are developed by LHS with input from SERC, and classroom-tested by the developers, then by expert teachers, and finally by a broader group of teachers from California and national sites. The module uses an issue-oriented approach to teaching concepts related to chemistry and energy topics. This approach teaches about hydrogen and fuel cells in the context of energy issues and demonstrates to students both the relevance of their science education to their lives and the role of scientists and engineers in solving practical problems.

Teachers who field-test the curriculum receive extensive professional development before they use the materials, and additional support as needed during use. This prepares the teachers to give thorough feedback on the curriculum and also informs future professional development activities. In addition, these early professional development workshops for field-test teachers help to identify teachers who will assist with dissemination and implementation of the published curriculum.

Results

The curriculum module addresses Education Technical Barriers A (Lack of Readily Available, Objective, and Technically Accurate Information) by providing information about hydrogen and fuel cells in a curriculum format that is usable by teachers and students in typical classrooms. The professional development work addresses Education Technical Barriers C (Disconnect between Hydrogen Information and Dissemination Networks) and D (Lack of Educated Trainers and Training Opportunities) by building on the dissemination networks of the LHS and partners and preparing teachers who will be able to provide professional development in their regions.

The national field-testing of the past year focused on Barrier E (Regional Differences), by testing the curriculum in a variety of settings. These included chemistry, physical science, physics, and environmental chemistry classrooms in parochial, public, and alternative high schools in urban and suburban settings. Many of the participating students were from populations under-represented in science, technology, engineering, and mathematics fields. Participating teachers included a mixture of those who had previously worked with the curriculum development team and those who had not, to ensure usability of the materials by a variety of teachers.

Thirteen teachers tested the two-week curriculum module with approximately 1,000 students in diverse high school classrooms in the San Francisco East Bay, California; Dublin, Ohio; and Bellevue, Washington during the 2008–2009 school year. While the majority of these students were in chemistry classes, participating classrooms also included physical science, physics, integrated science, and advanced placement environmental science. Figure 1 shows students in a San Francisco East Bay school that first used the curriculum during the past school year. In order to measure success (Barrier F), feedback was collected from participating teachers. Three teachers provided verbal feedback to the project via phone or face-to-face meetings, while 10 teachers completed an online feedback survey. The online survey includes questions about the curriculum module as a whole and about each of the six curriculum activities. Feedback was generally positive about the module, with many constructive suggestions for improving specific activities. For example, Figure 2 summarizes feedback on students' engagement with the module. All teachers indicated that they would teach the core activities of the module again. One or more teacher representatives from each location also participated in phone, email, or face-to-face meetings with the project staff to provide further input on the module. They also provided input on how to adapt the materials for diverse learners and for each of the five high school subjects in which it was taught.

FIGURE 1. High School Students Conduct a HyTEC Curriculum Activity

FIGURE 2. Teacher Survey Response: Student Engagement

A new group of teachers, representing additional national sites, will implement the curriculum in 2009–2010. In June 2009, these teachers joined a three-day professional development workshop conducted by project staff and held at the Lawrence Berkeley National Laboratory's Center for Science and Engineering Education. The workshops address Education Technical Barriers C (Disconnect between Hydrogen Information and Dissemination Networks) and D (Lack of Educated Trainers and Training Opportunities) by providing teachers with an in-depth professional development experience on the science of hydrogen and fuel cells, applications of fuel cells, and the use of the curriculum. Nineteen participants from five states will help to address technical barrier E (Regional Differences), by providing feedback on the use of the curriculum in states and school districts that each have specific science standards and student demographics. Participants included five teachers from the Los Angeles area (Los

Angeles and Santa Ana school districts), four from the San Francisco East Bay (representing four districts), seven from Connecticut (representing five districts), and one each from Evans, Georgia; Columbia, South Carolina; and New York City (Bronx). These teachers work in a variety of schools, including technical and agricultural programs, comprehensive public and parochial schools, a magnet school, and a selective private school. Many of the participating schools are located near hydrogen demonstration projects and hope to connect the curriculum to local activity related to hydrogen and transportation. Several of the teachers will be sharing the curriculum and what they have learned with others in their schools and districts. As in last year's workshops, participants conducted the curriculum activities and explored the equipment (see Figure 3), heard scientific presentations, participated in question and answer sessions with workshop leaders, and went on a half-day field trip to Alameda-Contra Costa Transit's hydrogen bus facility. They were also given ample time to provide feedback and suggestions and to discuss with each other the design of the curriculum and how they will implement the activities to best meet the needs of their student populations. In the workshop evaluation, participants ranked aspects of the professional development workshop on a scale from 1 (not adequate) to 5 (excellent). The results of the workshop evaluation are presented in Table 1. The teachers' comments about the workshop reflected the positive rankings, and included:

"Surpasses anything else I have done by far."

"This was one of the best workshops I have attended."

"This was *real* training with *real* people here to learn. Very encouraging."

To the extent possible, teacher leaders working with the project will contribute to future state, regional, and national science teacher conference presentations.

FIGURE 3. Summer 2009 Teacher Professional Development

TABLE 1. Professional Development Evaluations

Aspect of conference	Score (out of 5)
Curriculum activities	4.7
Activity presentations	4.7
Scientific presentations	4.6
Field trip to AC Transit	4.3
Schedule	4.7
Conference arrangements	4.8
Comparison to other workshops*	4.7

*The question asked: Compared to other workshops and professional development sessions I have attended, overall I would rank this one as. . .

Commercialization of the kit has begun. In December 2008, the project entered into a contractual agreement with Lab-Aids, Inc., who will produce the print and kit materials and market and sell the final curriculum. Lab-Aids, Inc. is Science Education for Public Understanding Program's publisher, has extensive experience in the K-12 science curriculum field, and is well known to school districts and science teachers nationwide. To date, they have produced prototype student electrolyzer components, which are currently being tested by SERC.

Conclusions and Future Directions

Conclusions

- The instructional materials and kit can be used by high school teachers working in a variety of science subject areas (chemistry, physics, physical science, integrated science, and advanced placement environmental science) and with diverse student populations. Students and teachers continue to be enthusiastic about these materials.
- The professional development workshop provides teachers with scientific and technical background and experiences that prepare them to use the curriculum activities and equipment for classroom instruction. In evaluations of the workshop, a diverse group of teachers rated the workshop 4.7 out of 5 in comparison to other workshops and professional development sessions they have attended.

- The curriculum and kit are ready for final revisions and commercialization in the coming year. Development of a key equipment piece, the student electrolyzer, has begun with the development and testing of prototypes prepared by Lab-Aids, Inc.

Future work will focus on:

- Preparing the commercial version of the HyTEC module. This will involve collaboration with Lab-Aids, Inc. on professional editing and page composition of the print materials in addition to development of final kit components, such as a student electrolyzer developed for this project.
- Expanding work with new school districts, and strengthening collaborations with current districts when possible.
- Presenting the project at science teacher conventions. So far, sessions have been accepted or are pending for Fall 2009 state teacher conferences in California, Texas, New York, Connecticut, and the National Science Teachers Association Southwestern Regional Conference in Arizona. The project will also be presented at the Spring 2010 National Science Teachers Association National Convention in Philadelphia.

FY 2009 Publications/Presentations

- Nagle, B. and L. Whitehurst. "The Chemistry of Hydrogen Fuel Cells." California Science Teacher's Association Conference, October 31, 2008, San Jose, California.
- Nagle, B. "Alternative Energy for Transportation: Hydrogen and Fuel Cells." National Science Teachers Association National Conference, March 20, 2009, New Orleans, Louisiana.
- Nagle, B. and J. Howarth. "Teach Chemistry with Hydrogen Fuel Cells." National Science Teachers Association National Conference, March 21, 2009, New Orleans, Louisiana.
- Zoellick, J. "HyTEC: "Introducing Hydrogen and Fuel Cells into High School Science Curriculum." National Hydrogen Association Conference, March 31, 2009, Columbia, South Carolina.

X.17 Hydrogen Knowledge and Opinions Assessment

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Subcontractor:

Opinion Research Corporation, Princeton, NJ

Project Start Date: April 2003

Project End Date: 2012

Contribution to Achievement of DOE Education Milestones

This project will contribute to achievement of the following DOE milestones from the Hydrogen Education section (Section 3.9) of the *Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan*:

- **Milestone 28:** Complete baseline assessment knowledge and opinion of hydrogen technologies for key target audiences. (4Q, 2004)
- **Milestone 29:** Evaluate knowledge and opinion of hydrogen technology of key target audiences and progress toward meeting objectives. (4Q, 2009)
- **Milestone 30:** Evaluate knowledge and opinion of hydrogen technology of key target audiences and progress toward meeting objectives. (4Q, 2012)
- **Milestone 31:** Evaluate knowledge and opinion of hydrogen technology of key target audiences. (4Q, 2015)

Objectives

- To measure the current (2008/2009) level of awareness and understanding of hydrogen and fuel cell technologies in five target populations:
 - General public
 - Students
 - State and local government agencies
 - Potential end users
 - Safety and codes officials
- To compare the current (2008/2009) level of awareness and understanding to results of the 2004 baseline.
- To analyze and summarize results for use in developing strategies and tactics for the Hydrogen Education subprogram.

Technical Barriers

This project addresses the following technical barriers from the Education section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (B) Mixed Messages
- (E) Regional Differences
- (F) Difficulty of Measuring Success

Accomplishments

- 2008 surveys of state and local government officials, end users, and students completed (July 2008).
- Analysis of survey results of the general public, state and local government officials, end users, and students completed (January 2009).
- Office of Management and Budget (OMB) approval to conduct the survey of safety and codes officials received (March 2009).
- Survey of safety and codes officials completed (June 2009).
- Analysis of survey results of safety and codes officials initiated (July 2009).

Introduction

Designing and maintaining an effective education program entails measuring baselines and periodically measuring what has been learned. The purpose of the Hydrogen Knowledge and Opinions Assessment project is to collect and analyze statistical data to establish baselines and changes in understanding and awareness about hydrogen, fuel cells, and the notion of a hydrogen economy. Statistical surveys that were conducted in 2004 are being conducted again in 2008/2009, and are envisioned to be fielded yet again in approximately 2011/2012. Scientific sampling is used to survey five populations: (1) the general public, ages 18 and

over (sample size = 1,000); (2) students, ages 12-17 (sample size = 1,000); (3) state and local government officials from state departments of transportation and environmental protection, state energy offices, and functionally similar personnel from cities and counties (sample size = 220); (4) potential hydrogen end-users in three business categories: transportation, businesses requiring uninterrupted power supplies, and industries with large power requirements (sample size = 601); and (5) safety and codes officials (sample size = 193).

The surveys are designed to accomplish specific objectives. Technical questions are posed to measure technical understanding and awareness of hydrogen technology. Opinion questions measure attitudes about safety, cost, the environment, performance, and convenience. Questions are posed to assess visions about the likelihood of various future applications of hydrogen technology. For most of the questions, “I don’t know” or “I have no opinion” are perfectly acceptable answers. Questions about information sources (teachers, friends, government, etc.) and media (radio, Internet, magazines, etc.) are posed to assess how energy technology information is received.

Approach

The approach to the current survey work is essentially the approach taken to the 2004 surveys. Current literature on hydrogen and fuel cell knowledge and attitudes was first reviewed to update a previous (2003) literature review [1]. The 2004 survey questionnaires were also reviewed and revised slightly for use in the 2008 surveys. With only a few exceptions, consistency was maintained across the years to facilitate unbiased comparisons with the previous surveys. A separate questionnaire for the safety and codes officials survey was developed. All of the surveys have similar but slightly different questionnaires, which include (in addition to routine demographic questions) a mixture of technical, opinion, and information resource questions. An example of one of the technical questions is “Hydrogen gas is toxic [true/false]?”. An example of an opinion question is “How would you feel if your local gas station also sold hydrogen? [Answers: frightened, uneasy, at ease, pleased, don’t know/no opinion.]”. An example of an information resource questions is “How often do you get energy information from different types of mass media (never, sometimes, frequently, don’t know)? [Answers: television, radio, Internet, newspapers, etc.]”.

A plan for quality assurance and data analysis was designed [2], and contracts were arranged with Opinion Research Corporation to conduct the survey interviews. A compendium of source materials was compiled [3]. Each survey component required the Paperwork Reduction Act approval by OMB. OMB approval was received in July 2007 to conduct the 2008

editions of the previously conducted survey components (general public, student, state and local government, and end-user surveys). Approval for the safety and codes component was received in March 2009. All survey components are conducted using computer assisted telephone interviewing. After the survey data has been collected and analyzed, a report will be prepared similar to the report for the 2004 surveys [4].¹

Results

Telephone interviewing for all five population groups of the 2008 survey is complete. A preliminary report providing draft analyses of the survey results for the first four surveys was provided to DOE in January 2009. A complete analysis will be performed on the results of all five surveys and documentation of the analysis will be provided by September 2009.

Overall, the average technical scores for the general public and government officials were remarkably similar to the 2004 results. The percentages of correct answers to eight core technical questions differed somewhat for individual questions, but the overall average percentage of correct answers was very similar. The average technical score for the student population increased by 4.5 percentage points. Average technical scores for the four surveys are shown in Table 1.

TABLE 1. Average Technical Scores by Population

Population	Sample size		Technical score (% correct)		Score difference (percentage points)
	2004	2008	2004	2008	
General public	889	1,000	35.2	35.2	+0.0
Students	1,000	1,004	35.3	39.8	+4.5
Government agencies	236	220	66.6	66.6	+0.1
End users	99	601	46.3	47.9	+1.6

Based on a draft analysis of results of the first four surveys (general public, students, state and local officials, and end users), technical understanding appears to influence opinions about safety. For all four survey groups, respondents with above-average scores on the technical questions were more likely to have an opinion (i.e., fewer “don’t know” responses), and for those respondents who expressed an opinion, their opinion was more likely to be positive. This relationship is shown for the general public in Figure 1.

Respondents to the general public survey were also more concerned about safety and cost than the environment, but more concerned about the environment than convenience or performance.

¹ See http://www1.eere.energy.gov/hydrogenandfuelcells/hydrogen_publications.html.

FIGURE 1. Positive association of technical understanding and opinions about safety, General Public Survey. Question Q8 (Question 3e in 2004): “How would you feel if your local gas station also sold hydrogen?” Respondents with above average technical scores are more likely to feel good (“at ease”; “pleased”) about it.

Student responses to statements about the potential benefits of hydrogen usage indicated that they generally agreed that the use of hydrogen would reduce emissions, improve air quality, and reduce U.S. dependence on foreign oil.

The state and local government survey indicated that over 60% of government officials and over half of end user respondents believe that hydrogen is as safe as gasoline or diesel fuels. Almost half of the government officials who were surveyed indicated that they had no plans for use of hydrogen or fuel cell technologies. Only 5% had plans to use hydrogen or fuel cell technologies within the next year. About 21% have plans for use in the next five years. These results are shown in Figure 2.

When asked about plans for using hydrogen and fuel cell technologies to meet their organizations’ energy needs, most end users responded that they plan to wait to see how the market develops before considering the use of hydrogen and fuel cells.

FIGURE 2. Plans to use hydrogen and fuel cell technologies, 2008 state and local government survey. Corresponding results for 2004 were similar.

The Internet is an important source for obtaining energy information for state and local officials as well as end users. Television remains a frequent source of energy information for the general public and students.

Additional results will be provided in the final report.

Conclusions and Future Directions

The hydrogen knowledge and opinions survey data collected for the five component populations will serve as reference points for (1) designing the Hydrogen Education subprogram, and (2) measuring changes in knowledge and opinions over time. As with the 2004 survey results, the results of the 2008/2009 surveys (including comparisons with the 2004 results) will be compiled into a data book or digest of the data, ultimately to serve in developing and adapting the Hydrogen Education subprogram. Designing the Education subprogram itself, however, is beyond the scope of the survey work.

Future work will include

- Analyzing and reporting on all survey findings (Fiscal Year 2009).
- Preparing presentations and other publications about the survey results.

References

1. Tykey Truett. *Literature Review for the Baseline Knowledge Assessment of the Hydrogen, Fuel Cells, and Infrastructure Technologies Program*, ORNL/TM-2003/258 (October 2003).

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X.18 H₂ Educate – Middle School Hydrogen Education Program

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Contract Number: DE-FG36-04GO14278

Subcontractors:

- Sentech, Inc., Bethesda, MD
- Los Alamos National Laboratory, Los Alamos, NM

Start Date: August 1, 2004

Projected End Date: July 30, 2010

hydrogen advocacy groups have produced educational information that in some areas would be considered more public relations information than education. This project addresses the need for educational materials that are available, objective, and accurate. Harnessing NEED's primary objective of objective information across its curriculum portfolio, the H₂ Educate materials are reviewed by subject matter experts, are made readily available via Web and partner Web sites as well as workshops, and are compared and contrasted with other hydrogen materials on a regular basis. This project's materials will continue to adapt as the need for additional and more robust materials becomes apparent.

B. Mixed Messages

This project was created and continues with the intent to provide cornerstone materials that address misconceptions, provide clarity of information, and link to accurate and available information when necessary and possible. The hydrogen community continues to have disparate views on certain subjects and the key messaging to use. NEED, with review from DOE, national labs, and subject matter experts, works to provide this project with common, clear language and messaging that students, teachers, and their families find useful and appropriate for age and knowledge level. NEED works to remove the misinformation from the diverse messages and provide a concise message for the intended audience.

C. Disconnect between Hydrogen Information and Dissemination Networks

NEED has capitalized on this disconnect and continues to work with information networks to become a stronger dissemination network – using local energy information networks to deliver training and information about hydrogen to the project's intended audience. Working with the information networks, NEED – acting as a dissemination network – provides a conduit for valuable and accurate hydrogen information for the 4-12 community. In addition, NEED has created its own information and dissemination network of 4-12 educators and the education community to deliver quality hydrogen education materials and training.

D. Lack of Educated Trainers and Training Opportunities

This project addresses the lack of educated trainers by providing professional development opportunities for teachers and energy professionals. These training opportunities provide participants with general

Objectives

- Collaborate to develop, design, and deliver a first-class, comprehensive middle school hydrogen education program that includes: training, classroom materials, technical and best-practices exchange, and evaluation.
- Design a program to link hydrogen science and technology and the concept of a hydrogen economy to the classroom.
- Educate the K-12 audience about hydrogen and fuel cell technologies to facilitate market acceptance.

Technical Barriers

This project addresses the following barriers from the Education section of the Hydrogen, Fuel Cells, and Infrastructure Technologies Multi-Year Program Plan:

A. Lack of Readily Available, Objective, and Technically Accurate Information

As awareness of hydrogen increases with increased media activity and inclusion in many state and local energy plans, there continues to be a lack of information that is readily available, accurate, and objective. Many

background, foundation knowledge, and expansion information for more technically advanced audiences. NEED trains a network of trainers to deliver the information in local communities as well.

E. Regional Differences

This project is adapted – in training methods and messaging – for local and regional differences – including proximity to hydrogen use and production. NEED’s programming is locally based, with local needs – both economic and educational – considered as programs are created. Regional differences in attitudes are addressed and discussed in training programs. In addition, regional access to hydrogen infrastructure is part of the program. Should hydrogen fueling stations, vehicles or fuel cells be nearby, the infrastructure is included in the programming.

F. Difficulty in Measuring Success

The project is measuring knowledge gain among its target audience and finding good results. Educational programs often have longer term impacts that are not easily measurable in the course of a month or year. True attitude change takes a longer period of time than information gain. In all cases, educators report a minimum of a 40% knowledge increase in hydrogen knowledge upon completion of the H₂ Educate workshop.

Contribution to Achievement of DOE Education Milestones

This project contributes to achievement of the following DOE Education milestones from the Education section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan – Task Six: Facilitate Development and Expansion Hydrogen Technology Education for Middle and High Schools:

- **Milestone 22:** Develop middle school teacher and student guides. (2Q, 2006)
- **Milestone 23:** Hold teacher workshops. (2Q, 2007 – 4Q, 2010)
- **Milestone 24:** Update middle school teacher and student guides. (4Q, 2008)
- **Milestone 25:** Update middle school teacher and student guides. (4Q, 2010)
- **Milestone 26:** Develop modules for high schools. (4Q, 2007)
- **Milestone 27:** Launch high school teacher professional development. (4Q, 2008 through 3Q, 2011)

Accomplishments

- In 50% of the time estimated, the team created the middle school H₂ Educate learning module. In spite of resource constraints, the project is 100% complete with its revised scope and now is in replication and outreach to more communities. The project is scalable and can be deployed incrementally with additional resources.
- The effort has garnered additional support from a variety of partners – state energy offices, Clean Cities organizations, utilities, energy companies and others.
- Over 7,000 teachers trained.
- Training programs completed in thirty-five states with additional training in 2009 due to renewed DOE funding.
- Pre-survey scores were five out of 15 correct on the survey of hydrogen knowledge and 13 out of 15 correct on post surveys.

Approach

The NEED Project brings its 29-year history in energy education, curriculum development, teacher training, and networking efforts to H₂ Educate for middle school curriculum development, teacher training, and the expansion of hydrogen understanding and knowledge in classrooms throughout the country. NEED, with Sentech, Inc. of Bethesda, Maryland as a key partner, launched a bold effort to exceed the U.S. Department of Energy’s expectations for a hydrogen education program in 2004 and have exceeded development calendar and outreach targets.

H₂ Educate and the activities undertaken as part of this project are the result of a collaborative effort among teachers, students, advisors, technical specialists, federal employees and professional educators. This effort brings together resources from NEED and its national partners and the U.S. Department of Energy, to capitalize on success, resources, networking opportunities, and curriculum development and delivery capabilities. Key elements of this project are NEED’s national network, a strong relationship with the National Association of State Energy Officials, and an annual budget capable of doubling the resources provided by this cooperative agreement. Making up this network are a conservatively estimated 65,000 classrooms touched by NEED materials and training each year.

Results

Results of the project continue to show success with pre-training survey results showing a five out

of 15 correct successful response and a post-training survey result showing a 13 out of 15 correct successful response.

Workshop outreach expanded from six training programs and several hundred teachers trained in the first year of the project with over 7,000 teachers trained by 2009. NEED works to deliver the H₂ Educate curriculum throughout the network of NEED schools and the schools they reach with educational outreach.

Curriculum materials are live on the NEED and U.S. Department of Energy Web sites and Web stats indicated substantial download activity.

Addition of hydrogen information and activities to the Energy Information Administration Kid's Page www.eia.doe.gov/kids (350,000 users per month).

Students and teachers show knowledge gain and deeper understanding of hydrogen knowledge.

On post-workshop surveys, teachers indicate feeling prepared to teach the materials in their classrooms.

Conclusions and Future Directions

H₂ educate programs this year continued to expand the reach of the project to middle schools throughout the country. Additional outreach via state energy offices has allowed additional programs to be delivered outside of the programs within the U.S. Department of Energy funding for this project. NEED has included the project in its partnership with the BP A+ for Energy Program and the Pacific Gas and Electric Solar Schools Program thus allowing several thousand teachers to benefit from the project training and curriculum materials.

The Virginia Department of Mines, Minerals and Energy and the Virginia General Assembly appropriated funding to provide teacher workshops and curriculum kits and materials to schools in Virginia in execution of the Virginia Hydrogen Roundtable recommendations.

Future Directions

- H₂ Educate sessions will be hosted at NEED's four National Energy Conferences for Educators in July and August 2009.
- H₂ Educate materials presented at 650 local teacher workshops.
- Work with other hydrogen partners to maximize reach of programs and materials – i.e. working with infrastructure grantees to provide educational resources.
- Continue incorporation of materials and programming into NEED's existing training initiatives.
- Annually update materials with new data and provide major changes to educational community.
- Addition of H₂ Educate Web site for materials, links and additional information.
- Deliver maximum number of hands-on resources to classrooms leveraging resources to do so. Expand partnerships with infrastructure grant recipients to provide outreach and education programming to additional communities.

XI. SMALL BUSINESS INNOVATION RESEARCH (SBIR) HYDROGEN PROGRAM NEW PROJECTS AWARDED IN FY 2009

XI.0 Small Business Innovation Research (SBIR) Hydrogen Program New Projects Awarded in FY 2009

The Small Business Innovation Research (SBIR) program provides small businesses with opportunities to participate in DOE research activities by exploring new and innovative approaches to achieve R&D objectives. The funds set aside for SBIR projects are used to support an annual competition for Phase I awards of up to \$100,000 each for about nine months to explore the feasibility of innovative concepts. Phase II is the principal research or R&D effort, and these awards are up to \$750,000 over a two-year period. Small Business Technology Transfer (STTR) projects include substantial (at least 30%) cooperative research collaboration between the small business and a non-profit research institution.

Table 1 lists the SBIR projects awarded in FY 2009 related to the Hydrogen Program. On the following pages are brief descriptions of each.

TABLE 1. FY 2009 SBIR Projects Related to the Hydrogen Program

Title	Company	City, State
XI.1 Integrated Membrane Water Gas Shift Reactor for Hydrogen Production (Phase I Project)	InnovaTek, Inc.	Richland, WA
XI.2 Development of a "4-in-1" Device for Cost Effective and Efficient Production of Hydrogen (Phase I Project)	Materials and Systems Research, Inc.	Salt Lake City, UT
XI.3 Advanced PEM Based Hydrogen Home Refueling Appliance (Phase I Project)	ElectroChem, Inc.	Woburn, MA
XI.4 Unitized Design for Home Refueling Appliance for Hydrogen Generation to 5000 psi (Phase I Project)	Giner Electrochemical Systems, LLC	Newton, MA
XI.5 Design, Optimization and Fabrication of a Home Hydrogen Fueling System (Phase I Project)	Lynntech, Inc.	College Station, TX
XI.6 Development of a Hydrogen Home Fueling System (Phase I STTR Project)	Materials and Systems Research, Inc.	Salt Lake City, UT
XI.7 Hydrogen by Wire-Home Fueling System (Phase I Project)	Proton Energy Systems	Wallingford, CT
XI.8 On-Line Measurement of PEM Electrolyzer Stacks (Phase I Project)	Reactive Innovations, LLC	Westford, MA
XI.9 Modeling of Hydrogen Dispensing Options for Advanced Storage (Phase I Project)	TIAX, LLC	Cambridge, MA
XI.10 Aqueous Phase Base-Facilitated-Reforming (BFR) of Renewable Fuels (Phase II Project)	Directed Technologies, Inc.	Arlington, VA
XI.11 Faradayic ElectroEtching of Stainless Steel Bipolar Plates (Phase II Project)	Faraday Technology, Inc.	Clayton, OH
XI.12 Anode Concepts for SO ₂ Crossover Reduction in the HyS Electrolyzer (Phase II Project)	Giner Electrochemical Systems, LLC	Newton, MA
XI.13 Power Generation from an Integrated Biofuel Reformer and Solid Oxide Fuel Cell (Phase II Project)	InnovaTek, Inc.	Richland, WA

PHASE I PROJECTS

XI.1 Integrated Membrane Water Gas Shift Reactor for Hydrogen Production

InnovaTek, Inc.
350 Hills Street
Suite 104
Richland, WA 99354-5511

This project will develop advanced membrane reactor technology for the production of clean hydrogen that can result in economic, energy, and environmental benefits by opening new avenues for energy production, reducing energy consumption, increasing capital productivity, and reducing waste and pollutants.

XI.2 Development of a “4-in-1” Device for Cost Effective and Efficient Production of Hydrogen

Materials and Systems Research, Inc.
5395 West 700 South
Salt Lake City, UT 84104

This project will lead to the development of an economical means to intensify hydrogen production processes for various applications such as transportation, petroleum refinery, military and residential use.

XI.3 Advanced PEM Based Hydrogen Home Refueling Appliance

ElectroChem, Inc.
400 West Cummings Park
Woburn, MA 01801

This project will develop a small appliance for refueling hydrogen vehicles by the homeowner that is low cost and uses inexpensive off-peak electricity to produce hydrogen from water. This appliance will reduce the infrastructure cost for development of the hydrogen vehicle market in both the near and long term.

XI.4 Unitized Design for Home Refueling Appliance for Hydrogen Generation to 5000 psi

Giner Electrochemical Systems, LLC
89 Rumford Avenue
Newton, MA 02466-1311

To enable the transition to a hydrogen economy, the successful implementation of a “unitized” electrolyzer design that can be used as a home refueling appliance will result in a safe, high-efficiency, low capital cost system that will provide competitively-priced hydrogen for fuel-cell vehicles.

XI.5 Design, Optimization and Fabrication of a Home Hydrogen Fueling System

Lynntech, Inc.
7610 Eastmark Drive
College Station, TX 77840

This project will identify infrastructure problems and system requirements to design and fabricate an affordable, safe and energy efficient home hydrogen fueling appliance. It is targeted to meet hydrogen refueling needs of the average U.S. traveler on a daily basis and has potential application as a backup power source in emergencies.

XI.6 Development of a Hydrogen Home Fueling System

STTR Project
Materials and Systems Research, Inc.
5395 West 700 South
Salt Lake City, UT 84104

This project provides a technical and economic means for development of hydrogen home fueling systems featuring hydrogen, power and heat tri-generation.

XI.7 Hydrogen by Wire-Home Fueling System

Proton Energy Systems
10 Technology Drive
Wallingford, CT 06492

One of the most attractive ways to implement a home hydrogen fueling station is the proton exchange membrane (PEM) water electrolysis hydrogen generator. PEM technology can generate the hydrogen fuel from renewable electricity and directly fill a vehicle at home in the user's garage.

XI.8 On-Line Measurement of PEM Electrolyzer Stacks

Reactive Innovations, LLC
2 Park Drive, Unit 4
Westford, MA 01886

This project will develop a sensor to assess the quality of membrane and electrode assemblies before they are incorporated into higher-value electrolyzers. The success of this product innovation will help lower the manufacturing cost for water electrolyzers targeted by the Department of Energy to generate hydrogen for transportation and stationary applications.

XI.9 Modeling of Hydrogen Dispensing Options for Advanced Storage

TIAX, LLC
15 Acorn Park
Cambridge, MA 02140-2301

On-board vehicle hydrogen storage volumetric and gravimetric targets have not been achieved with 35 MPa compressed hydrogen storage. Five promising advanced storage categories have been identified by the DOE, and this project will develop hydrogen dispensing configurations and cost estimates for each storage option.

PHASE II PROJECTS

XI.10 Aqueous Phase Base-Facilitated-Reforming (BFR) of Renewable Fuels

Directed Technologies, Inc.
3601 Wilson Blvd.
Suite 650
Arlington, VA 22201

XI.11 Faradayic ElectroEtching of Stainless Steel Bipolar Plates

Faraday Technology, Inc.
315 Huls Drive
Clayton, OH 45315

XI.12 Anode Concepts for SO₂ Crossover Reduction in the HyS Electrolyzer

Giner Electrochemical Systems, LLC
89 Rumford Aveue
Newton, MA 02466-1311

XI.13 Power Generation from an Integrated Biofuel Reformer and Solid Oxide Fuel Cell

InnovaTek, Inc.
350 Hills Street, Suite 104
Richland, WA 99354-5511

XII. Acronyms, Abbreviations and Definitions

°C	Degrees Celsius	$\mu\text{A}/\text{cm}^2$	Micro ampere(s) per square centimeter
°F	Degrees Fahrenheit	μg	Microgram(s)
Δ	Change, delta	μm	Micrometer(s); micron(s)
$\sim$	Approximately	μM	Micromolar
$\approx$	Equals approximately	μmol	Micromole(s)
$>$	Greater than	$\mu\Omega\text{-cm}^2$	Micro-ohm(s) - square centimeter
$\geq$	Greater than or equal to	μV	Micro volt(s)
"	Inch(s)	Ω	Ohm(s)
$\leq$	Less than or equal to	$\Omega\text{-cm}^2$	Ohm-square centimeter
$<$	Less than	A	Ampere, amps
#	Number	Å	Angstrom
%	Percent	A_o	Arrhenius constant, $\text{ml}/(\text{cm}^2\text{-min-atm}^{1/2})$
®	Registered trademark	AAO	Anodic aluminum oxide
\$	U.S. Dollars	AB	Ammonia borane, NH_3BH_3
1-D, 1D	One-dimensional	ABH_2	Ammonium borohydride, NH_4BH_4
2-D, 2D	Two-dimensional	ABI	Automated ball indentation; agent-based investment
2-FPTf	2, fluoropyridinium triflate	ABM	Agent-based modeling
3-D, 3D	Three-dimensional	ABMS	Agent-based modeling and simulation
1Q	First quarter of the fiscal year	ABPBI	Poly(2,5-benzimidazole)
2Q	Second quarter of the fiscal year	AC	Activated carbon; air-cooled; alternating current
3Q	Third quarter of the fiscal year	A/C	Anode/cathode
4Q	Fourth quarter of the fiscal year	ACF	Activated carbon fibers
6F	Hexafluorinated (biphenol A) sulfonated poly(arylene ether sulfone)	A/cm^2	Amps per square centimeter
6FCN-x	HexaFluoro bisphenol A based disulfonated polybenzonitrile (H+ form) (x denotes degree of sulfonation)	ACN	Acetonitrile
6FK	Partially fluorinated poly(arylene ether ketone)	ACR	Autothermal cyclic reforming
6F-x	HexaFluoro bisphenol A based disulfonated polySulfone (H+ form) (x denotes degree of sulfonation)	ACS	American Chemical Society
8YSZ	8 mol% yttria-stabilized zirconia	AC Transit	Alameda-Contra Costa Transit
$^{11}\text{B-NMR}$	Boron 11 nuclear magnetic resonance	AE	Alkaline earth
$^{19}\text{FNMR}$	^{19}F Fluorine nuclear magnetic resonance	AECL	Atomic Energy Canada, Limited
$\alpha\text{-AlH}_3$	Alpha polymorph of aluminum hydride	AEO	Annual Energy Outlook
ΔB_a	The difference in magnetic induction at high and low applied magnetic fields	AER	Absorption-enhanced reforming; all-electric range
ΔG	Gibbs free energy of reaction	AES	Auger electron spectroscopy
ΔH	Enthalpy of reaction, Enthalpy of hydrogenation	AFB	Airfoil bearing
ΔH°_f	Standard heat of formation	AFM	Atomic force microscopy; anti-ferromagnetic
ΔP	Pressure drop, pressure change	AFP	Automated fiber placement
λ	Lambda, hydration number	AFV	Alternative fuel vehicle
μA	Micro ampere(s)	Ag	Silver
		AgCl	Silver chloride
		A-h	Amp-hour
		AIBN	Azobisisobutyl nitrile

XII. Acronyms, Abbreviations and Definitions

AICHE	American Institute of Chemical Engineers	ATP	Adenosine triphosphate
AISI	American Iron & Steel Institute	ATPase	Adenosine triphosphatase
AK	Alkali	ATR	Autothermal reformer; autothermal reforming; attenuated total reflection
Al	Aluminum	ATR-FTIR	Attenuated total reflectance Fourier transform infrared
Al*	Aluminum particles catalyzed with titanium	Au	Gold
Al ₂ O ₃	Aluminum oxide	a.u.	Arbitrary units
Al-AB	Aluminum ammonia-borane	AuS	Gold sulfide
AlCl ₃	Aluminum chloride	AuSnO _x	Gold supported on hydrous tin oxide
ALD	Atomic layer deposition	AuTiO _x	Gold supported on titanium oxide
AlH ₃	Aluminum hydride; alane	Avg	Average
ALS	Advanced Light Source at Lawrence Berkeley National Laboratory	ΔB _a	The difference in magnetic induction at high and low applied magnetic fields
AM 1.5	Air Mass 1.5 solar illumination	B	Boron
AMBH	Ammine metal borohydride	B ₂ O ₃	Boron oxide; diboron trioxide
AMR	Annual merit review; active magnetic regenerator	Ba	Barium
AMRL	Active magnetic regenerative liquefier	BAC	Bond additivity correction
ANL	Argonne National Laboratory	barg	Bar gauge
ANS	American Nuclear Society	bcc	Body-centered cubic
ANSI	American National Standards Institute	BCN	Boron carbon nitride
A ₀	Arrhenius constant, ml/(cm ² -min-atm ^{1/2})	BCP	Block copolymers
AP	Advanced prototype	BDC	Benzenedicarboxylate
AP	Anode polarization	BDS	Broadband dielectric spectroscopy
APC	Adaptive process control	Be	Beryllium
APCI, APCi	Air Products and Chemicals, Inc.	BeD-XRD	Beryllium dome X-ray diffraction
APR	Aqueous-phase reforming	BES	Basic Energy Sciences office within the DOE Office of Science
APRxn	Aqueous phase reaction	BET	Brunauer-Emmett-Teller surface area analysis method
APU	Auxiliary power unit	B-G	Boron-doped graphitic material
Ar	Argon	B-H	Borohydride; boron/hydrogen bond
Arb, arb.	Arbitrary	BH ₄	Borohydride
ARET	Alternative and renewable energy technologies	Bi	Bismuth
As	Arsenic	BILI	Bio-derived liquid fuels
a-Si	Amorphous silicon	BisSF	Bisphenol-Sulfone
a-SiC	Amorphous silicon carbide	BM	Ball-milled; ball mill
a-SiGe	Amorphous silicon germanium	BMG	Bulk metallic glasses
ASM	American Society of Metals	bmimBF ₄	1-butyl-3-methyl-imidazolium tetrafluoroborate
ASME	American Society of Mechanical Engineers	bmimCl	1-butyl-3-methyl-imidazolium chloride
ASPEN	Modeling software, computer code for process analysis	BmimOTf	1-butyl-3-methyl-imidazolium triflate
ASR	Area-specific resistance	bmimPF ₆	1-butyl-3-methyl-imidazolium hexafluorophosphate
ASTM	ASTM International	BMPFFP	1-butyl-1-methyl-pyrrolidinium tris(pentafluoroethyl)trifluorophosphate
AT	Ammonia triborane	BN	Boron-nitrogen
at%	Atomic percent	BNHx	Dehydrogenated ammonia-borane
atm	Atmosphere		

BNL	Brookhaven National Laboratory	C ₃ H ₈	Propane
BNNT	Boron nitride nanotubes	C&S	Codes and Standards
B-O	Any oxidized boron species, borate	Ca	Calcium
Boc	Tert-butoxycarbonyl	CA	Carbon aerogel
B(OH) ₃	Boric acid	CaBr ₂	Calcium bromide
BOL	Beginning of life	CaCO ₃	Calcium carbonate
BOMD	Born-Oppenheimer Molecular Dynamics	CAD	Computer-aided design
BOP, BoP	Balance of plant	CAE	Computer-assisted engineering
¹¹ B-NMR	Boron 11 nuclear magnetic resonance	CaFCP	California Fuel Cell Partnership
BP	Formerly British Petroleum, British Petroleum America Production Company	CAFE	Corporate Average Fuel Economy
BPDC	Biphenyldicarboxylate	CaI	<i>Clostridium acetobutylicum</i> hydrogenase
bpe	Bis(4-pyridyl)ethane	CALPHAD	Calculation of phase diagrams
BPEE	1,2-bipyridylethene	Caltech	California Institute of Technology
BPP	Bipolar plate	CaO	Calcium oxide
BPPPO	Biphenol-based phenyl phosphine oxide	CARB	California Air Resources Board
BPPPO-35	Biphenol-based phenyl phosphine oxide copolymer, 35% molar fraction of disulfonic acid unit (35% level of sulfonation)	CaS	Calcium sulfide
BPS	Ballard Power Systems; bi phenyl sulfone	CBM	Conduction band minimum
BPS100	Fully disulfonated poly(arylene ether sulfone)	CBN	Carbon-boron-nitrogen
BPSH	Block polysulfone ether polymers; bi phenyl sulfone: H form	CBS	Casa Bonita strain; complete basis set
BPSH-x	BiPhenyl based disulfonated polySulfone (H+ form) (x denotes degree of sulfonation)	cc	Cubic centimeter(s)
BPSH-30	Biphenyl sulfone H form, 30% molar fraction of disulfonic acid unit (30% level of sulfonation)	CCA	Charge control agent
BPVE	Perfluorocyclobutane-biphenyl vinyl ether	CCAT	Connecticut Center for Advanced Technology, Inc.
BPVE-6F	Perfluorocyclobutane-biphenyl vinyl ether hexafluoroisopropylidene	CCD	Charge-coupled device
BPY	2,2'-bipyridine	cCH ₂	Cryo-compressed hydrogen
BPY	4,4'-bipyridine	CCM	Catalyst-coated membrane; coordinate measuring machine
Br	Bromine	cc/min	Cubic centimeters per minute
Br ₂	Diatomic bromine	ccp	Cubic close-packing
BSC	Bi-electrode supported cell	CCSD(T)	Coupled cluster theory with single and double excitations plus a perturbative correction for triple excitations
BTB	1,3,5-benzenetribenzoate	Cd	Cadmium
BTU, Btu	British thermal unit(s)	CD	Compact disk; charge depleting; cathode dewpoint
Bu ₃ SnCl	Tributyltin chloride	CDC	Carbide-derived carbon
Bu ₃ SnSnBu ₃	Hexabutylstannane	cDNA	Complementary DNA
BV	Benzyl viologen	CDO	Code development organization
BxHy	Polyhedral boranes	CDP	Composite data product
C	Carbon; Coulomb; coulomb	CdS	Cadmium sulfide
C ₂ H ₄	Ethylene	Ce	Cerium
C ₂ H ₆	Ethane	CEA	Commissariat à l'Énergie Atomique
		CEMM	Compressor-expander motor module
		CeO ₂	Ceric oxide
		CEQA	California Environmental Quality Act
		CF	Carbon fiber; carbon foam
		CFC	Chlorofluorocarbon

XII. Acronyms, Abbreviations and Definitions

CFCC	Colorado Fuel Cell Center	COS	Carbon oxysulfide; carbonyl sulfide
CFD	Computational fluid dynamics	COSMO/RS	COnductor like Screening MOdel for Realistic Solvents (computational method)
CFM, cfm	Cubic feet per minute	CoT	City of Taylor
CGM	Charge-generating material	CoTMPP	Cobalt tetramethoxyphenyl porphyrin
CGO	Cerium gadolinium oxide, Gd-doped CeO ₂	CoTPP	Cobalt tetraphenyl porphyrin
CGS	Copper gallium diselenide	COx	Oxides of carbon
CGSe ₂	Copper gallium diselenide	c _p	Specific heat
CH	Hydrogenated graphene	CPO	Coordination polymer Oslo
CH ₂	Compressed hydrogen gas	CPO, CPOX	Catalytic partial oxidation
CH ₄	Methane	CP-Ti	Commercially pure titanium
CHHP	Combined heat, hydrogen, and power	CPU	Computer processing unit
Chl	Chlorophyll	Cr	Chromium
CHP	Combined heat and power	CRBJT	Combined reverse-Brayton Joule-Thompson
CHSCoE	Chemical Hydrogen Storage Center of Excellence	CRW	Clipped random wave
CI	Compression ignition	Cs	Cesium
CIGS	Copper indium gallium diselenide	CS	Charge sustaining
CIGSe ₂	Copper indium gallium diselenide	CSA	Canadian Standards Association; cell stack assembly
CIRRUS	Cell Ice Regulation & Removal Upon Start-up	CSD	Compression-storage-delivery
CIS	CuInSe (alloy of copper, indium, and selenium)	CSM	Colorado School of Mines; combined structure & material
Cl	Chlorine	CSR	Catalytic steam reforming; compressive stress relaxation
cm	Centimeter	CT	Compact tension
cm ²	Square centimeter	CTA	Charge transfer agent
CMAQ	Community multiscale air quality	CTC	Concurrent Technologies Corporation
CMO	Conductive metal oxides	CTE	Coefficient of thermal expansion
CMR	Composite membrane reactor	CTFE	Chlorotrifluoroethylene
CMS	Carbon molecular sieve	CTTRANSIT	Connecticut Transit
CMU	Carnegie Mellon University	CTV	Chevron Technology Ventures LLC
CMWNT	Carbon multi-walled nanotube	Cu	Copper
CN	Carbon-nitrogen	Cu ₂ O	Cuprous oxide
CNG	Compressed natural gas	CU	University of Colorado
CNM	Crystalline nanoporous material	cu. in.	Cubic inch
CNMS	Center for Nanophase Materials Sciences	CUMC	Coordinatively unsaturated metal centers
CNT	Carbon nanotube	CuO	Cupric oxide, copper(II) oxide
Co	Cobalt	CV	Cyclic voltammetry; cyclic voltammogram
CO	Carbon monoxide	CVD	Chemical vapor deposition
CO ₂	Carbon dioxide	CVS	Chemical vapor synthesis
COD	Chemical oxygen demand	CWRU	Case Western Reserve University
CoE	Center of Excellence	CY	Calendar year
COF	Covalent-organic framework	CZO	Ceria-zirconia
COF ₂	Carbonyl fluoride	d	Day(s)
CONCAWE	Conservation of Clean Air and Water in Europe	D ₂	Deuterium
COPV	Composite Overwrapped Pressure Vessel		

DA	Dubinin-Astakhov	DP	Dew point
DAC	Donor-acceptor-complex	DPD	Dissipative particle dynamics
DADB	Diammoniate of diborane, [(NH ₃) ₂ BH ₂][BH ₄]	DRIFTS	Diffuse reflectance infrared Fourier transform spectroscopy
DAS	Data acquisition system	DSC	Differential scanning calorimetry
dB(A)	Decibel(s) A scale	DSM	Dimensionally stable membrane
DBPDSA	1, 4-dibromo phenylene 2, 5-disulfonic acid	DST	Dynamic stress test
DC	Direct current	DTA	Differential thermal analysis
d_{DR}	Dubini-Radushkevich average micropore diameter	DTI	Directed Technologies, Inc.
DDR	A zeolite structure code	DVBPC	Divinyl aryl ether monomer
DEDP	Distance Education Degree Program	DVD	Digital video disk
DEF	Diethylformamide	DVT	Design verification test
Deg, deg	Degree	e ⁻	Electron
DEGDBE	Diethylene glycol dibutyl ether	E, Ea	Activation energy, kJ/mol
ΔB_a	The difference in magnetic induction at high and low applied magnetic fields	$E_0 \times E_1$	Utilization efficiency of incident solar light energy
DEP	Department of Environmental Protection	E_{ad}	Hydrogen adsorption heat
DF	Digital fabrications	E-BOP	Electrical balance of plant
DFM	Design for manufacturing; degree of fuel mixing	EBSD	Electron backscatter diffraction
DFMA [®]	Design for Manufacturing and Assembly	EC	Evaporative-cooled, efficiency of conversion
DFT	Density functional theory	ECA	Electrochemical area
DHBC	2,5-dihydroxybenzene dicarboxylate	ECE-WP29/ GRPE	United Nations Economic Commission for Europe, World Forum for Harmonization of Vehicle Regulations, and Working Party on Pollution and Energy Program
DI	Deionized; de-ionized water	ECS	Equilibrium crystal shape
DIG	Digoxigenin	ECSA	Electrochemically active surface area; Electrochemical surface area
DLC	Diamondlike carbon	ECST	College of Engineering, Computer Science and Technology
dL/g	Deciliters per gram	EDA	Ethylene diamine
DMAc	Dimethyl acetamide	EDAX	Manufacturer of energy dispersive X-ray hardware and software
DMDS	Dimethyldisulfide	EDBB	Ethylenediamine bisborane
DME	Dimethyl ether; dimethoxyethane	edmimCl	2-ethyl-1,3-dimethyl-imidazolium ethylsulfate
DMEA	Dimethylethylamine	EDS	Energy dispersive X-ray spectroscopy, energy dispersive spectrum
DMF	n, n-di-methyl formamide	EDTA	Ethylenediamine tetraacetic acid
DMFC	Direct methanol fuel cell	EDX	Energy dispersive X-ray
dmimMeSO ₄	1,3-dimethyl-imidazolium methylsulfate	EE	Electrical engineering
dmpe	Dimethylphosphinoethane	EELS	Electron energy loss spectroscopy
DMPO	5,5-Dimethylpyrroline-N-oxide	EERE	U.S. DOE Office of Energy Efficiency and Renewable Energy
DMSO	Dimethyl sulfoxide	EFR-AHJ	Emergency first responder-authorities having jurisdiction
DMT	Dimethyltrityl	e.g.	exempli gratia, for example
DMTHF	Dimethyltetrahydrofuran		
DNA	Deoxyribonucleic acid		
DOD	U.S. Department of Defense		
DOE	U.S. Department of Energy		
DOT	Department of Transportation		
DOT/NHTSA	Department of Transportation/National Highway Traffic Safety Administration		

XII. Acronyms, Abbreviations and Definitions

EH&S	Environmental Health and Safety	FCFP	FreedomCAR and Fuel Partnership
EHC	Electrochemical hydrogen compressor	FCPP	Fuel cell power plant
EIA	Energy Information Administration of the U.S. Department of Energy	FCS	Fuel cell system
EIHP	European Integrated Hydrogen Project	FCTES ^{QA}	Fuel Cell Testing, Safety and Quality Assurance (an international effort to harmonize fuel cell testing procedures)
EIS	Electrochemical impedance spectroscopy	FCTESTNET	Fuel Cell Testing and Standardization Network
El	Elongation to fracture	FCV	Fuel cell vehicle
eNMR	Electrochemical nuclear magnetic resonance	Fd	Ferredoxin
EOL	End of life	FDA	Finite difference analysis
EPA	U.S. Environmental Protection Agency	FDS	Filter difference spectrometer
EPDM	Ethylene propylene diene monomer	Fe	Iron
ES	Energy storage	FE	U.S. DOE Office of Fossil Energy
ESEM	Environmental scanning electron microscopy	Fe ₂ O ₃	Ferric oxide
ESI-MS	Electrospray ionization mass spectrometry	FEA	Finite element analysis
ESR	Electron spin resonance	FEP	Fluorinated ethylene propylene; Teflon [®]
ESU	Electrostatic unit of charge	FF	Fill factor
et al.	et alii, and others	FFOV	Fossil-fuel onroad vehicle
ET	Event tree	FHWA	Federal Highway Administration
ETA	Event tree analysis	FIB	Focused ion beam
etc.	et cetera, and so on	FLACS	FLame ACceleration Simulator
ETFE	Ethylene-tetrafluoroethylene	FLiNaK	LiF-NaF-KF eutectic salt
EtOH	Ethanol	FMEA	Failure modes and effects analysis
ETR	Electron transfer rate	¹⁹ FNMR	¹⁹ Fluorine nuclear magnetic resonance
EU	European Union	FOM	Federated object model; figure of merit
eV	Electron volt	FP	Fuel processor
EVS	Electric Vehicle Symposium and Exhibition	FPA	Fluoroalkyl phosphonic and phosphinic acids
EW	Enthalpy wheel; equivalent weight	fpi	Fins per inch
EWH	Enthalpy wheel humidifier	fpm	Feet per minute
EXAFS	Extended X-ray absorption fine structure analysis	FMVSS	Federal Motor Vehicle Safety Standards
F	Fluorine; Faraday constant, the amount of electric charge in one mole of electrons (96,485.3383 coulomb/mole)	FRP	Fiber-reinforced polymer
F ⁻	Fluorine ion	FRR	Fluoride release rate
FA	Furfyl alcohol	FSEC	Florida Solar Energy Center
FAT	Fleet Analysis Toolkit	F-SPEEK	Fluorosulfonic acid of polyetheretherketone
FBMR	Fluidized bed membrane reactor	ft	Feet
FC	Fuel cell	FT	Fault tree
FCB	Fuel cell bus	ft ²	Square feet
fcc	Face-centered cubic	ft ³	Cubic feet
FCCP	Carbonyl cyanide m-chlorophenylhydrazone	FTA	Federal Transit Administration; fault tree analysis
FCE	FuelCell Energy	FT-IR, FTIR	Fourier transform infrared
FCEV	Fuel cell electric vehicle	FTIR-ATR	Fourier transform infrared attenuated total reflection
		FTO	Fluorine-doped tin oxide
		FTP	Federal Test Procedure

FW	Filament winding	GNF	Graphite nanofiber
FWHM	Full width at half maximum	GOS	Global ocean sampling
FY	Fiscal year	GPa	Gigapascal(s)
ΔG	Gibbs free energy of reaction	GPC	Gel permeation chromatography
g	Gram; acceleration of gravity	GPS	Global positioning system
G	Graphite	GRC	Glass-reinforced concrete
Ga	Gallium	GREET	Greenhouse gases, Regulated Emissions and Energy use in Transportation model
GA	General Atomics	g/s	Grams per second
GaAs	Gallium arsenic	GTI	Gas Technology Institute
gal	Gallon	GTR	Global Technical Regulations
GaP	Gallium phosphide	GUI	Graphical user interface
GATOR-GCMOM	Gas, Aerosol, Transport, Radiation, General Circulation, Mesoscale, and Ocean Model	GV	Gasoline vehicle
GB	Gigabyte	GW	Product of the Green's function, G, and the energy, W; an approximation permitting practical calculation of excitation energies in metals, semi-conductors and insulators
GC	Gas chromatograph	GWe	Gigawatt(s) electric
g/cc	Grams per cubic centimeter	ΔH	Enthalpy of reaction, Enthalpy of hydrogenation
GCLP	Grand-canonical linear programming	ΔH°_f	Standard heat of formation
GCMC	Grand Canonical Monte Carlo	h, hr, hrs	Hour(s)
GCMS	Gas chromatograph mass spectroscopy	H	Hydrogen
Gd	Gadolinium	H ⁺	Proton
GDC	Gadolinium-doped ceria	H ⁻	Hydride
GDE	Gas diffusion electrode	H ₂	Diatomic hydrogen
GDL	Gas diffusion layer	H2A	Hydrogen Analysis project sponsored by DOE
GDM	Gas diffusion media	H ₂ BPyDC	2,2'-bipyridine-5,5'-dicarboxylic acid
GDS	Galvanodynamic scan	H ₂ cat	Catechol; 1,2 dihydroxybenzene
Ge	Germanium	H ₂ -FCS	Stationary fuel cell system designs that co-produce hydrogen
Gen I	First generation	H ₂ (hfipbb)	4,4'-(hexafluoroisopropylidene) bis(benzoic acid)
GES	Giner Electrochemical Systems, LLC	H ₂ ICE, H2-ICE	Hydrogen internal combustion engine
GGA	Generalized gradient approximation	H ₂ O	Water
GGE, gge	Gasoline gallon equivalent	H ₂ O ₂	Hydrogen peroxide
GH ₂	Gaseous hydrogen	H ₂ oba	4,4'-oxybis-benzoic acid
GHG	Greenhouse gas	H2QWG	DOE Hydrogen Quality Working Group
GHSV	Gas hourly space velocity	H ₂ S	Hydrogen sulfide
GIC	Graphite intercalation complex	H ₂ SO ₄	Sulfuric acid
GIS	Geographic information system	H ₃ BBC	1,3,5-tris(4'-carboxy[1,1'-biphenyl]-4-yl-) benzene
GJ	Gigajoule(s)	H ₃ BTB	4,4',4''-benzene-1,3,5-triyl-tribenzoic acid
g/kW	Gram(s) per kilowatt	H ₃ PO ₄	Phosphoric acid
GLACD	Glancing angle co-deposition	HAADF	High-angle annular dark-field
GLAD	Glancing angle deposition	HAADF-STEM	High angle annular dark field scanning transmission electron microscopy
GLY	Glycerol		
Glyme	Dimethoxyethane		
gm	Gram(s)		
GM	General Motors		
gm/day	Gram(s) per day		
g/min	Gram(s) per minute		

XII. Acronyms, Abbreviations and Definitions

HAMMER	Hazardous Materials Management and Emergency Response	HKUST	1 Cu ₃ (1,3,5-benzenetricarboxylate) ₂
HATCI	Hyundai-KIA America Technical Center Inc.	HLA	High level architecture
HAVO	Hawaii Volcanoes National Park	HMC	Hyundai Motor Company
HAZ	Heat affected zone	HNEI	Hawaii Natural Energy Institute
HAZID	Hazard Identification Analysis	HNO ₃	Nitric acid
HAZOP	Hazards and Operational Safety Analysis, hazards and operability analysis	HOMO	Highest occupied molecular orbital
H-Bcat	Catecholborane where boron is bound to catecholate dianion and a hydride (B-H)	hp	Horsepower
HBr	Hydrogen bromide	HP	High-pressure
HBTU	o-Benzotriazol-1-yl-N,N,N',N'-tetramethyluronium hexafluorophosphate	HPA	Heteropoly acid
HCl, HCL	Hydrochloric acid; hydrogen chloride	HPLC	High performance liquid chromatography
HClO ₄	Perchloric acid	HPRD	Hydrogen pressure relief device
HCO ₃ ⁻	Bicarbonate	hr	Hour(s)
hcp	Hexagonal close-packed	HRL	Hughes Research Laboratory, HRL Laboratories, LLC
HD	Deuterium hydride	HRL meso-C	Mesoporous carbon synthesized by HRL using pyrolysis of mesoporous polymer
HDPE	High-density polyethylene	HRTEM	High-resolution transmission electron microscopy
HDSAM	Hydrogen Delivery Scenario Analysis Model	HRXRT	High-resolution X-ray tomography
He	Helium	HSC	Database name derived from the letters for enthalpy, entropy and heat capacity
HE	Hydrogen embrittlement	HSCoE	Hydrogen Sorption Center of Excellence
HEHP	High-energy, high-pressure	HSDC	Hydrogen Secure Data Center
HES	Hydrogen energy station	HSECoE	Hydrogen Storage Engineering Center of Excellence
HEV	Hybrid electric vehicle	HSO ₄	Bisulfate anion
HEX	Heat exchange	HSRP	Hydrogen Safety Review Panel
Hf	Hafnium	HSU	Humboldt State University; hydrogen separation unit
HF	Hydrofluorhydric acid; hydrogen fluoride; Hartree Fock	HT	High-temperature
HFB	Hexafluorobenzene	HTE	High-temperature electrolysis
HFCIT	Hydrogen, Fuel Cells and Infrastructure Technologies Program	HTF	Heat transfer fluid, Hydrogen test facility
HFCT	Hydrogen and fuel cell technology	HTGR	High-temperature gas-cooled reactor
HFCV	Hydrogen fuel cell vehicle	HTHX	High-temperature heat exchanger
HFP	Hexafluoropropylene; 1,1,1,3,3,3 hexafluoro-2-propanol	HTM	High-temperature membrane; hydrogen transport membrane
HFR	High-frequency impedance; high-frequency resistance	HTMWG	High Temperature Membrane Working Group
HFS	Hydrogen fueling station	HTP	High throughput
HGMs	Hollow glass microspheres	HTSC	High temperature superconductor
HHV	Higher heating value	HTSE	High temperature steam electrolysis
HI	Hydrogen iodide; hydriodic acid	HT-WGS	High-temperature water-gas shift
HIC	Hydrogen-induced cracking	HTXRD	High-temperature X-ray diffraction
HiCON	High CO Conversion Process	H _{upd}	Hydrogen underpotential deposition
HIPOC	Hydrogen Industry Panel on Codes	HWCVD	Hot-wire chemical vapor deposition
HIx	Blend of hydrogen iodide, iodine, and water	HWFET	Highway Fuel Economy Test
		HX	Heat exchanger

HyDRA	Hydrogen Demand and Resource Analysis	INS	Inelastic neutron scattering
HyDS-ME	Hydrogen Deployment System Modeling Environment	IPA	Isophthalate
HYPER	HYdrogen PERmitting	IPCC	Intergovernmental Panel on Climate Change
HyS	Hybrid sulfur	IPCC SRES	IPCC Special Report on Emissions Scenarios
HYSYS®	Process simulation software by AspenTech, computer code for flowsheet analysis	IPCE	Incident photon conversion to electrons, incident photon conversion efficiency
Hz	Hertz	IPES	Inverse photoemission spectroscopy
i	Current density (mA/cm ²)	IPG	Installation Permitting Guidance
I	Current	IPHE	International Partnership for the Hydrogen Economy
I ₂	Diatomic iodine	IPPSS	Integrated Power Plant/Storage System
IC	Internal combustion	IPTG	Isopropyl β-D-1-thiogalactopyranoside
ICC	International Code Council	iR	Internal resistance; voltage loss due to resistance
ICE	Internal combustion engine	Ir	Iridium
ICEV	Internal combustion engine vehicle	IR	Infrared
ICP	Inductively coupled plasma	IRDA	Infrared data acquisition
ICPAE	Inductively coupled plasma atomic emission	IRMOF	Isorecticular metal organic framework
ICP-AES	Inductively coupled plasma atomic emission spectroscopy	ISIS	Pulsed neutron and muon source located at the UK Rutherford Appleton Laboratory
ICP-MS	Inductively coupled plasma mass spectrometry	ISO	International Organization for Standardization
ICP-OES	Inductively coupled plasma optical emission spectroscopy	ITM	Ion transport membrane
ICR	Interfacial contact resistance	ITO	Indium tin oxide
ICSD	Inorganic Crystal Structure Database	ITP	Indium tin phosphate
ID	Inside diameter	ITS	Institute of Transportation Studies
i.e.	id est, that is	IV	Current-voltage
IE	Initiating event	J	Current; Joule(s)
IEA	International Energy Agency	JARI	Japan Automobile Research Institute
IEA-HIA	International Energy Agency Hydrogen Implementing Agreement	JFK	John F. Kennedy (airport)
IEC	International Electrotechnical Commission; ion exchange capacity	JHQTF	Joint Hydrogen Quality Task Force (U.S. Fuel Cell Council)
IFC	International Fire Code	JMFC	Johnson Matthey Fuel Cells, Inc.
IGT	Institute of Gas Technology	JP-8	Jet fuel (Propellant 8)
IHPV	Internally heated high-pressure vessel	JPL	Jet Propulsion Laboratory
IINS	Inelastic incoherent neutron scattering	Jsc	Short circuit current density
IIT	Illinois Institute of Technology	JV	Current density-voltage
IL	Ionic liquid	K	Sievert's constant, ml/(cm ² -min-atm ^{1/2}); Kelvin, absolute temperature; Potassium
ILS	Integrated laboratory scale	kÅ	1,000 angstroms
In	Indium	kA/m ²	Kilo-ampere(s) per square meter
In., in	Inch	KBr	Potassium bromide
in ²	Square inch	kcal	Kilocalorie(s)
INERI	International Nuclear Energy Research Initiative	kcal/mol	Kilocalorie(s) per mole
INL	Idaho National Laboratory	KeV	Kilo electron volt(s)

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kg	Kilogram(s)	LDA	Local density approximation
kg/d	Kilogram(s) per day	LDV	Light-duty vehicle
kg/hr	Kilogram(s) per hour	LED	Light emitting diode
kg/m ³	Kilogram(s) per cubic meter	LEL	Lower explosion limit
KH	Potassium hydride	LFG	Land fill gas
KHTC	Potassium-promoted hydrotalcite	LFL	Lower flammability limit
kHz	Kilohertz	L/h, l/h	Liter(s) per hour
KIA	Kia Motor Company	LH ₂ , LH ₂	Liquid hydrogen
K _{IC}	Fracture toughness	LHC	Light-harvesting chlorophyll
K _{IH}	Fracture toughness measured in hydrogen gas	LHS	Lawrence Hall of Science
kJ	Kilojoule(s)	LHSV	Liquid hourly space velocity
kJ/mol	Kilojoule(s) per mole	LHV	Lower heating value
km	Kilometer(s)	Li	Lithium
KMC	Kia Motors Corporation	Li ₃ N	Lithium nitride
KOH	Potassium hydroxide	Li-AB	Lithium amidoborane; Li-NH ₂ -BH ₃
kPa	Kilopascal(s)	LiBH ₄	Lithium borohydride
kph	Kilometer(s) per hour	LIBS	Laser-induced breakdown spectroscopy
K _{TH}	Hydrogen-assisted crack growth threshold	LiH	Lithium hydride
Kth	Fracture toughness threshold	LIM	Liquid injection molding; liquid injection moldable
kW	Kilowatt(s)	LLC	Limited Liability Company
kW _e	Kilowatt(s) electric	LLNL	Lawrence Livermore National Laboratory
kWh	Kilowatt-hour(s)	LMDS	Laser modulation differential spectroscopy
kWh/kg	Kilowatt-hour(s) per kilogram	L/min, l/min	Liter(s) per minute
kWh/L	Kilowatt-hour(s) per liter	LMWO	Lanthanum molybdenum tungsten oxide (<i>e.g.</i> , La ₂ Mo _{1.8} W _{0.2} O _{9-x})
kW/kg	Kilowatt(s) per kilogram	LN ₂	Liquid nitrogen
kWt	Kilowatt(s) thermal	LNG	Liquefied natural gas
λ	Lambda, hydration number	LOHC	Liquid organic hydrogen carrier
L, l	Liter(s)	LPG	Liquefied petroleum gas
La	Lanthanum	LPM	Liter(s) per minute
LAOX	Lanthanum molybdenum oxide (<i>e.g.</i> , La ₂ Mo ₂ O ₉)	LQ*	Dehydrogenated liquid carrier
LANL	Los Alamos National Laboratory	LQ*H ₂	Hydrogenated liquid carrier
LAO	Lanthanum-modified alumina	LSC	Lanthanum strontium cobalt oxide, (La, Sr)CoO ₃ , strontium-doped lanthanum cobaltite; La _{0.8} Sr _{0.2} CoO _{3+δ}
LAX	Los Angeles International Airport	LSCF	Lanthanum strontium cobalt iron oxide, (La, Sr)(Co, Fe)O ₃
lb	Pound(s)	LSCF7328	La-Sr-Cu-Fe-O
LBM	Lattice Boltzmann method	LSCM	Lanthanum strontium chromium manganese oxide, (La, Sr)(Cr, Mn)O ₃
lbmol	Pound-mole(s)	LSCr	Lanthanum strontium chromium oxide, (La, Sr)CrO ₃
LBNL	Lawrence Berkeley National Laboratory	LSDA	Local spin density approximation
LC	Liquid carrier	LSM	Lanthanum strontium manganese oxide, (La, Sr)MnO ₃ , strontium-doped lanthanum manganite, La _{0.8} Sr _{0.2} MnO _{3+δ}
LCA	Life cycle assessment		
LCC	La _{0.7} Ca _{0.3} CrO _{3-δ}		
LCH ₂	Hydrogenated liquid carrier; liquid to compressed hydrogen		
LC-MS	Liquid chromatography-mass spectroscopy		
L/D	Length to diameter ratio		

LST	Lanthanum strontium titanium oxide, (La, Sr)TiO ₃	MeAB	Methylamine borane
LSV	Lanthanum strontium vanadate; linear sweep voltammetry	MEAM	Modified embedded atom method
LT	Low-temperature	MEC	Microbial electrolysis cell, Minimum explosive concentration
LTDMS	Laser induced thermal desorption mass spectrometry	MECS	Microtechnology-based energy and chemical systems
LUMO	Lowest unoccupied molecular orbital	MEMS	Micro-electro-mechanical systems
LV	Louver fins	MeOH	Methanol
m	Meter(s)	MEOP	Maximum expected operating pressure
M	Mole; molar; million	meq	Milliequivalents
m ²	Square meter(s)	meq/g	Milliequivalents/gram
m ² /g	Square meter(s) per gram	MeV	Mega electron volt
m ² /s	Square meter(s) per second	MFC	Microbial fuel cell, Mass flow controller
m ³	Cubic meter(s)	MFE	Membrane-free extract
M41	Arkema's second-generation membrane candidate	MFI	A zeolite structure code
M43	Arkema's third-generation membrane candidate	Mg	Megagram(s)
M70	Arkema's fourth-generation membrane candidate	μg	Microgram(s)
mΩ	Milli-ohm(s)	mg	Milligram(s)
MΩ	Mega-ohm(s)	MgCl ₂	Magnesium chloride
mΩ/cm ²	Milli-ohm(s) per square centimeter	mg/cm ²	Milligram(s) per square centimeter
mA	Milliamps (s)	MgH ₂	Magnesium hydride
μA	Micro-ampere(s)	MgH ₂ @C	MgH ₂ incorporated in carbon scaffold
M-AB	Metal ammonia-borane	MgO	Magnesium oxide
mA/cm ²	Milliamp(s) per square centimeter	Mg(OH) ₂	Magnesium hydroxide
μA/cm ²	Micro-ampere(s) per square centimeter	mgPt/cm ²	Milligram (s) of platinum per square centimeter
MALDI	Matrix-assisted laser desorption/ionization	MH	Membrane humidifier; metal hydride
MAS	Magic angle spinning	MHC	Metal hydride-based compressor
MAS ¹¹ B-NMR	Magic angle spinning boron-11 nuclear magnetic resonance spectroscopy	MHCoE	Metal Hydride Center of Excellence
MAS-NMR	Magic angle spinning nuclear magnetic resonance	MHz	Megahertz
MB	Megabyte	mi	Mile(s)
MBE	Molecular beam epitaxy	MI	Mixed inocula
MBMS	Molecular beam mass spectrometry	MIE	Minimum ignition energy
MBWR	Modified Benedict Webb Rubin	MIEC	Mixed ionic and electronic conduction
MC	Monte Carlo; microchannel	mi/kg	Mile(s) per kilogram
mC ²	Multi-component composite (membrane)	mil	Millimeter(s)
mC-cm ⁻²	MilliCoulomb(s) per square centimeter	min	Minute(s)
MCFC	Molten carbonate fuel cell	MIT	Massachusetts Institute of Technology
MD	Molecular dynamics	MiTi®	Mohawk Innovative Technologies Inc.
MDES	Methyl-diethoxy silane	MJ	Megajoule(s)
mdip	5,5'-methylene-di-isophthalate	mL, ml	Milliliter(s)
MEA	Membrane electrode assembly	ML	Monolayer
		μm	Micrometer(s); micron(s)
		μM	Micromolar
		mm	Millimeter(s)
		mM	Millimolar
		MMBtu	Million British thermal units

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MMOF	Metal-organic framework	mW	Milliwatt(s)
mmol	Millimole(s)	MW	Megawatt(s); molecular weight
μmol	Micromole(s)	mW/cm ²	Milliwatt(s) per square centimeter
MMSCFD	Million standard cubic feet/day	MWCNT	Multiple-wall carbon nanotube
Mn	Manganese	MWe	Megawatt(s) electric
Mn ₂ O ₃	Manganese oxide	MWh	Megawatt-hour(s)
M-N-H	Amide/imide	MWNT	Multi-wall carbon nanotube
MnO	Manganese oxide	MWOE	Midwest Optoelectronics, LLC
Mo	Molybdenum	MWth	Megawatt(s) thermal
MO	Molecular orbital; metal oxide	MYPP	Multi-Year Program Plan (the HFCIT Program's Multi-Year Research, Development and Demonstration Plan), Multi-year product plan
MOF	Metal-organic framework		
mol	Mole(s)		
mol%	Mole percent	N	Normal (e.g., 1N H ₃ PO ₄ is 1 normal solution of phosphoric acid); Nitrogen atom; Newton (unit of force)
mol/min	Mole(s) per minute		
mΩ	Milli-ohm(s)		
MΩ	Mega-ohm(s)	N112	Nafion [®] 1100 equivalent weight, 2 millimeter thick membrane
mΩ/cm ²	Milli-ohm(s) per square centimeter	N ₂	Diatomic nitrogen
μΩ-cm ²	Micro-ohm(s) - square centimeter	N ₂ O	Nitrous oxide
MoPc	Molybdenum phthalocyanine	Na	Sodium
MOZART	Model for OZone And Related Trace species chemical-transport model of the global atmosphere	Na ₂ S	Sodium sulfide
		Na ₃ AlH ₆	Trisodium hexahydroaluminate
MP2	Second-order Moller-Plesset perturbation theory	NaAlH ₄	Sodium aluminum hydride; sodium tetrahydroaluminate; sodium alanate
MPa	Megapascal (s)	NaBH ₄	Sodium borohydride
MPG, mpg	Mile(s) per gallon	NaBO ₂	Sodium metaborate
mph	Mile(s) per hour	NaCl	Sodium chloride
MPL	Microporous layer	NADH	(reduced) Nicotinamide adenine dinucleotide
MPMC	Massively Parallel Monte Carlo	Nafion [®]	Registered Trademark of E.I. DuPont de Nemours
MPPO	Modified poly(phenylene oxide)	NaH	Sodium hydride
MPPT	Maximum power point tracker	NaOH	Sodium hydroxide
MRI	Magnetic resonance imaging	NAS	National Academy of Sciences
ms	Millisecond(s)	NASA	National Aeronautics and Space Administration
MS	Mass spectroscopy, mass spectrometry	NASFM	National Association of State Fire Marshals
M-S	Mott-Schottky		
MSA	Metropolitan statistical area; methanesulfonic acid	Nb	Niobium
mS/cm	Milli-Siemen(s) per centimeter	N/cm ²	Newton(s) per square centimeter
MS-EVB	Multi-state empirical valence bond method for simulating proton transport via the Grotthuss shuttling mechanism	NCN	Nano capillary network
MSM	Macro-System Model	NCNR	NIST Center for Neutron Research
MSR	Membrane steam reformer	nc-Si:H	Nanocrystalline silicon
MTA	Metric tonne per annum	NCSR	National Center of Scientific Research
mtorr	Millitorr	ND	Not determined at this time
μV	Micro volt(s)	NDC	New delivery concept
mV	Millivolt(s)	NDE	Non-destructive examination
MV	Methyl viologen		

NE	U.S. DOE Office of Nuclear Energy, Science and Technology	NPM	Nanostructured polymeric materials; non-precious metal
NEC	National Electrical Code	NPPD	n-phenyl-phenylenediamine
NEDO	New Energy and Industrial Technology Development Organization (Japan)	NPT	Normal pressure and temperature
NEED	National Energy Education Development Project	NPV	Net present value
NEPA	National Environmental Policy Act	NR ₃	Tertiary amine
NERI	Nuclear Energy Research Initiative	NRC	National Research Council
NERI-C	Nuclear Energy Research Initiative-Consortium	NREL	National Renewable Energy Laboratory
NESSHY	Novel Efficient Solid Storage of Hydrogen	NSF	National Science Foundation
NETL	National Energy Technology Laboratory	NSTF	Nano-structured thin-film
NFC	Near-frictionless carbon	NSTFC	Nano-structured thin film catalyst
NFM	Nanoporous framework material	NTE	Negative thermal-expansion
NFPA	National Fire Protection Association	NV	Neutron vibrational
ng	Nanogram	NVS	Neutron vibrational spectroscopy
NG	Natural gas	O	Oxygen
NGNP	Next Generation Nuclear Plant	O ₂	Diatomic oxygen
NG-SR	Natural gas steam reforming	O/C	Oxygen-to-carbon ratio
NGV	Natural gas vehicle	OCP	Open circuit potential
NH ₃	Ammonia	OCSD	Orange County Sanitation District
NHA	National Hydrogen Association	OCV	Open-circuit voltage
NHE	Normal hydrogen electrode	o.d., OD	Outer diameter
NHI	Nuclear Hydrogen Initiative	ODA	Oxygenated form of diamine
NHTSA	National Highway Traffic Safety Administration of the U.S. Department of Transportation	OEC	Oxygen evolving complex
Ni	Nickel	OEM	Original equipment manufacturer
NILS	Normal interstitial lattice sites	OER	Oxygen evolution reaction
NiMH	Nickel metal hydride	OH ⁻	Hydroxyl radical
NIST	National Institute of Standards and Technology	OHFCIT	Office of Hydrogen, Fuel Cells, and Infrastructure Technologies
NL	Normal liter(s)	Ω	Ohm(s)
nm	Nanometer(s)	Ω-cm ²	Ohm-square centimeter
NM	Noble metal	O&M	Operation and maintenance
Nm ³	Normal cubic meter(s)	OMC	Ordered mesoporous carbon
nmol	Nanomole(s)	ORNL	Oak Ridge National Laboratory
NMP	N-methylpyrrolidone	ORNL-HTML	Oak Ridge National Laboratory High Temperature Materials Laboratory
NMR	Nuclear magnetic resonance	ORR	Oxygen reduction reaction
NO ₂	Nitric oxide	OSC	Oxygen storage capability; Orlando Science Center
NOA	Norland Optical Adhesive	OSHA	U.S. Occupational Safety and Health Administration
NO _x	Oxides of nitrogen	OSM	Oregon Steel Mills, Optical scatterfield microscopy
NPB	Neopentyl benzene	OSU	Ohio State University; Oregon State University
NPC	Nanoporous carbon	o-SWNH	Oxidized single-walled nanohorn
NPD	Neutron powder diffraction	OTM	Oxygen transport membrane
NPDF	Neutron powder diffraction	ΔP	Pressure drop, pressure change
		P	Phosphorus; pressure

XII. Acronyms, Abbreviations and Definitions

$p\text{-H}_2$	Para-hydrogen	PEI	Polyetherimide
Pa	Pascal(s)	PEKK	Poly (ether ketone ketone)
PA	Phenylacetylene; polyamide	PEM	Polymer electrolyte membrane; proton exchange membrane
PAA	Poly(acrylic acid)	PEMFC	Polymer electrolyte membrane fuel cell; proton exchange membrane fuel cell
PAFC	Phosphoric acid fuel cell	PEN	Polyethylene naphthalate
PAN	Peroxyacetyl nitrate	PEO	Poly(ethylene oxide)
PANI	Polyaniline	PES	Polyether sulfone; polyethersulfone-polyimide copolymer
PA/PBI	Phosphoric-acid-doped polybenzimidazole	PET	Polyethylene terephthalate
PAR	Photosynthetically-active radiation	PF	Phenolic
PAS	Photoactive semiconductor	PFA	Perfluoroalkoxy (a type of fluoropolymer); polyfurfuryl alcohol
PAW	Projector augmented wave	PFAC	PFA-derived carbon
Pb	Lead	PFCS	Poly-generative fuel cell systems
PB	Polyborazylene	PFD	Process flow diagram
PbA	Lead acid	PFG-NMR	Pulse field gradient nuclear magnetic resonance
PBE	Perdew-Burke-Ernzerhof	PFGSE	Pulse field gradient spin echo
PBI	Polybenzimidazole	PFSA	Perfluorinated sulfonic acid; perfluorosulfonic acid
PbO	Lead oxide	PG	Propylene glycol
PBPDSA	poly(biphenylene disulfonic acid)	PGAA	Prompt gamma activation analysis
P-C	Pressure-composition	PGE	Platinum group element
PC	Polycarbonate	PGM	Precious group metal; platinum group metal
PCE	Perchloroethylene	PGSE	Pulsed-field gradient spin-echo
PCF	Polycarbonate film	$p\text{-H}_2$	Para-hydrogen
PCHD	Poly(cyclohexadiene)	Ph_3SnCl	Triphenyltin chloride
PCI	Pressure-composition isotherm	$\text{Ph}_3\text{SnSnPh}_3$	Hexaphenyldistannane
PCM	Power control module	PHEV	Plug-in hybrid vehicle
P-C-P	Phosphorus-carbon-phosphorus	PhOH	Phenol
PCR	Polymerase chain reaction	PI	Principal investigator; polyimide
PCT, P-C-T	Pressure-concentration-temperature	P&ID	Piping and instrumentation diagram; process and instrumentation diagram
Pd	Palladium	PIL, pIL	Protic ionic liquid
PD	Power density	PIM, pIM	Protic ionic membrane
PdAg	Palladium-silver alloy	PLC	Programmable logic controller
PdCu, Pd-Cu	Palladium-copper alloy	PLLA	Poly-L-lactic acid
PdCuTM	Palladium copper transition metal	PM	Precious metal such as platinum
PDF	Probability density function; pair distribution function	PM_{10}	Particulate matter with diameters of 10 micrometers or less
PDU	Process development unit	$\text{PM}_{2.5}$	Particulate matter with diameters of 2.5 micrometers or less
PE	Polyethylene, proton conductor	PNNL	Pacific Northwest National Laboratory
PEC	Photoelectrochemical; photoelectrochemical cell	pO_2	Oxygen partial pressure
PECVD	Plasma-enhanced chemical vapor deposition	POC	Proof of concept
PEEK	Polyether ether ether ketone		
PEFC	Polymer electrolyte fuel cell		
PEG	Polyethylene glycol		
PEGS	Prototype electrostatic ground state		

POCOP	<i>P,P</i> -bis(1,1-dimethylethyl)-,3-[[<i>bis</i> (1,1-dimethylethyl)phosphino]oxy]phenyl ester	PTA	Phosphotungstic acid
POF	Polymeric-organic frameworks	Pt/AC/BC/IRMOF-8	Isorecticular metal organic framework (MOF) doped with platinum supported on activated carbon, and further coupled to MOF with a bridging compound
POM	Polyoxometallate	Pt/AX-21	Pt-doped microporous carbon AX-21
POSS	Polyhedral oligomeric silsesquioxane	Pt/C	Platinum/carbon
POX	Partial oxidation	PTFE	Teflon® – poly-tetrafluoroethylene
PP	Polyphosphazene, polypropylene	Pt-FePO	Platinum iron phosphate
PPA	polyphosphoric acid	Pt-MM	Platinum group mixed metal
ppb	Part(s) per billion	Pt-NH	Platinum decorated carbon nano-horns
ppbv	Part(s) per billion by volume	PtO	Platinum oxide
PPDSA	Poly (p-phenylene disulfonic acid)	PtO ₂	Platinum dioxide
PPI	Pore(s) per inch	PtRu	Platinum ruthenium
ppm, PPM	Part(s) per million	Pt-SWNH	Platinum decorated single-walled nanohorns
ppmv	Part(s) per million by volume	Pt-TaPO	Platinum tantalum phosphate
ppmw	Part(s) per million by weight	PTW	Pump-to-wheels
PPO	Phenyl phosphine oxide	PV	Photovoltaic
PPS	Polyphenylenesulfide	PVA	Polyvinyl
PPSA	Poly (p-phenylene sulfonic acid); partial pressure swing adsorption	PVC	Polyvinyl chloride
PPSU	Polyphenylsulfone	PVD	Physical vapor deposition
PPy	polypyrrole	PVDF	Polyvinylidene fluoride
Pr	Praseodymium	PVP	Polyvinylpyrrolidone
PRD	Pressure relief device	PVPP	Polyvinyl pyridinium phosphate
PrOx	Preferential oxidation	PVT, P-V-T	Pressure-Volume-Temperature
PRSV	Peng-Robinson Stryjek-Vera	PyC	4-pyrazole carboxylate
PS	Proton sponge (bis- (dimethylamino) naphthalene); polysiloxane	PzDC	2,8-pyrazabole dicarboxylate
PSA	Pressure swing adsorption, adsorber	Q	Neutron momentum transfer
PSAT	Powertrain Systems Analysis Toolkit, a vehicle simulation software package developed at Argonne National Laboratory	Q1, Q2, Q3, Q4	Quarters of the fiscal year
PSD	Particle size distribution, pore size distribution	QC	Quality control; quantum corrections
PSEPVE	Perfluoro (4-methyl-3,6-dioxaoct-7-ene) sulfonyl fluoride	QCM	Quartz crystal microbalance
psi, PSI	Pound(s) per square inch	QENS	Quasielastic neutron scattering
psia	Pound(s) per square inch absolute	Q-HOP MD	A version of a molecular dynamics simulation that includes quantum chemistry calculations
psid	Pound(s) per square inch differential	QLRA	Qualitative risk analysis
psig, PSIG	Pound(s) per square inch gauge	QMC	Quantum Monte Carlo
PSU	Pennsylvania State University	QRA	Quantitative risk assessment
Pt	Platinum	Qst	Isosteric heats of adsorption
PT	Phosphazene trimer	R	Universal or ideal gas constant, 8.314472 J · K ⁻¹ · mol ⁻¹
P-T	Pressure-temperature	RA	Reduction of area
Pt ₃ Co	Platinum-cobalt alloy	Raman	Spectroscopic technique
Pt ₃ Fe	Platinum-iron alloy	R&D	Research and development
Pt ₃ Ni	Platinum-nickel alloy	RD&D, R,D&D	Research, development & demonstration
		RDE	Rotating disk electrode

XII. Acronyms, Abbreviations and Definitions

RDU	Reactor development unit	SDE	SO ₂ -depolarized electrolyzer
REC	Renewable energy credit	SDO	Standards development organization
RF, rf	Radio frequency	Se	Selenium
RGA	Residual gas analyzer (analysis)	SE	Secondary electron
Rh	Rhodium	sec	Second(s)
RH	Relative humidity	SEC	Size exclusion chromatography
RHE	Reference hydrogen electrode; reversible hydrogen electrode	SEM	Scanning electron microscopy, scanning electron microscope
RNA	Ribo nucleic acid	SENT	Single edge notch tension
rpm, RPM	Revolution(s) per minute	SEO	State Energy Office
RPN	Risk priority number	SERC	Schatz Energy Research Center
RPSA	Rapid pressure swing adsorption	SF ₆	Sulfur hexafluoride
RRC	Regional resource center	SFC2	SrFeCo _{0.5} O _x
RRDE	Rotating ring disc electrode	SFT	Sr-Fe-Ti oxide
RSA	Random sequential adsorption	SHE	Standard hydrogen electrode
RT	Room temperature	Si	Silicon
Ru	Ruthenium	Si ₃ N ₄	Silicon nitride
s	Second(s)	S-I	Sulfur-iodine
S	Siemen(s); Sulfur	SI	Sulfur-iodine cycle
SA	Surface area	SiC	Silicon carbide
SAE	Society of Automotive Engineers	SiCN	Silicon carbonitride
SAFC	Solid acid fuel cell	SiO ₂	Silicon dioxide
SAH	Sodium aluminum hydride	sL	Standard liter (0°C, 1 atm)
SANS	Small angle neutron scattering	slpm, slm, sL/min	Standard liter(s) per minute
SAXS	Small angle X-ray scattering	SMEs	Subject matter experts
S _{BET}	BET specific surface area	SMR	Steam methane reformer; steam methane reforming
SBH	Sodium borohydride	SMUD	Sacramento Municipal Utility District
SBIR	Small Business Innovation Research	Sn	Tin
SBU	Secondary building units	SNL	Sandia National Laboratories
Sc	Scandium	SNS	Spallation neutron source
S/C	Steam to carbon ratio	SNTT	Spiral notch torsion test
SCCM, sccm	Standard cubic centimeter(s) per minute	SLAC	Stanford Linear Accelerator Center
SCE	Saturated calomel electrode	SLPH, slph	Standard liter(s) per hour
SCF, scf	Standard cubic feet, supercritical fluid	SLPM, slpm	Standards liter(s) per minute
SCFD, scfd	Standard cubic feet per day	SnO	Tin oxide
SCFH, scfh	Standard cubic feet per hour	SnO ₂	Tin dioxide
SCFM, scfm	Standard cubic feet per minute	SO ₂	Sulfur dioxide
S/cm	Siemen(s) per centimeter	SO ₃	Sulfur trioxide
SCR	Selective catalytic reduction, semi-conductor rectifier	SOC	State-of-charge
ScSZ	Scandia-stabilized zirconia	SOEC	Solid oxide electrolysis cell; solid oxide electrolyzer cell
SD	Standard deviation	SOFC	Solid oxide fuel cell
SDAPP	Sulfonated Diels-Alder polyphenylene	SOFEC	Solid oxide fuel-assisted electrolysis cell
SDAPPe	Sulfonated Diels-Alder polyphenylene ether	SOW	Statement of work
SDC	Samarium doped ceria	SOx	Oxides of sulfur
SDD	Si-drift detector		

sPAES	Sulfonated poly(arylene ether sulfone)	TBAB	Tetra- <i>n</i> -butylammonium bromide
SPEEK	Sulfonated poly(ether ether ketone)	TBABh	Tetra- <i>n</i> -butylammonium borohydride
SPEKK	Sulfonated polyether(ether ketone ketone)	TBA ₂ B ₁₂ H ₁₂	Tetra- <i>n</i> -butylammonium dodecahydrododecaborate
SPEX	Type of milling machine	TBA-PF ₆	Tetra- <i>n</i> -butylammonium hexafluorophosphate
sPOSS	Sulfonated octaphenyl polyhedral oligomeric silsesquioxanes	TBD	To be determined
sq. in.	Square inch(es)	TBMD	Tight-binding molecular dynamic
Sr	Strontium	TC	Thermocouple
SR	Steam reformer; steam reforming	TCCR	Transparent, conducting and corrosion resistant
SR-M	Steam reformer membrane	TCD	Thermal conductivity detector
SRNL	Savannah River National Laboratory	TCPDU	NREL 150 kWt thermochemical pilot development unit
SrO	Strontium oxide	TDLAS	Tunable diode laser absorption spectroscopy
SrTiO ₃	Strontium titanate, the proton conducting material	TDV	Technology demonstration vehicle
SS	Stainless steel	Te	Tellurium
SSA	Specific surface area	TEA	Triethylamine
SSAWG	Storage System Analysis Working Group	TEA ₂ B ₁₂ H ₁₂	Triethylammonium dodecahydrododecaborate
SSC	Structure, system, and component	TEAA	Triethylamine alane adduct
SSI	Single substrate inocula	TEAB	Tetraethyl ammonium borohydride
SSR [®]	Stackable Structural Reactor	TEAH	Tetraethylammonium hydroxide
SSRL	Stanford Synchrotron Radiation Laboratory	TEAMS	tetraethylammonium methane sulfonic
SSRS	Solid-state reactive-sintering	TED	Triethylene-diamine
STCH	Solar Thermochemical Hydrogen	TEDA	Triethylenediamine
STEM	Scanning transmission electron microscopy; science, technology, engineering, and mathematics	TEM	Transmission electron microscopy
STH	Solar-to-hydrogen	TEOM	Tapered element oscillating microbalance
STM	Scanning tunneling microscopy	TEOS	Tetra-ethoxy silane
STMBMS	Simultaneous thermogravimetric modulated beam mass spectrometer	Tf	Trifluoromethane sulfonate, or triflate anion (CF ₃ SO ₃ ⁻)
STP	Standard temperature and pressure	TFA	Trifluoromethanesulfonic acid
STS	Scanning tunneling spectroscopy	TFAc	Trifluoroacetate
STTR	Small Business Technology Transfer	TFE	Tetrafluoroethylene
S _u	Ultimate tensile strength	TFMPA	Trifluoromethylphosphonic acid
SWCNT	Single-walled carbon nanotube	TFMSA	Trifluoromethane sulfonic acid
SWNH	Single-walled nanohorn	TF-RDE:	Thin film rotating disk electrode
SWNT	Single-wall nanotube	tf-Si	Thin film silicon
SwRI [®]	Southwest Research Institute [®]	TFSI	bis(Trifluoromethylsulfonyl)imide
S _y	Yield strength	TFVE	Trifluorovinyl ether
T	Temperature; ton; tonne; Tesla (unit of magnetic induction)	TG	Thermogravimetric, Theory Group
T _{1bar}	Temperature at which equilibrium pressure of hydrogen is 1 bar for a hydrogen exchange reaction	TGA	Thermal gravimetric analysis; thermogravimetric analysis; thermogravimetric analyzer
TAMU	Texas A&M University	TGA-DSC	Thermo-gravimetric analysis-differential scanning calorimetry
TaPO	Tantalum phosphate	TGA-MS	Thermogravimetric analysis-mass spectrometer

XII. Acronyms, Abbreviations and Definitions

THF	Tetrahydrofuran	UCI	University of California, Irvine
Ti	Titanium	UCLA	University of California, Los Angeles
TiCl ₃	Titanium trichloride	UCONN	University of Connecticut
TiF ₃	Titanium trifluoride	UCSB	University of California, Santa Barbara
TiH ₂	Titanium hydride	UEA	Unitized electrode assembly
Ti-IRMOF-16	Titanium (Ti) intercalated IRMOF-16	UEL	Upper explosive limit
TIO	Technology improvement opportunities	UFL	Upper flammability limit
TiO ₂	Titanium dioxide (anatase)	UH	University of Hawaii
<i>Tla</i>	Truncated light-harvesting chlorophyll antenna	UHP	Ultra-high purity
<i>tla1</i>	Mutant of the Tla1 gene (GenBank Assession No. AF534570)	UHV	Ultra-high vacuum
<i>tlaR</i>	Mutant of unknown gene with a truncated light-harvesting chlorophyll antenna	UIUC	University of Illinois, Urbana-Champaign
<i>tlaX</i>	Mutant of unknown gene with a truncated light-harvesting chlorophyll antenna	UL	Underwriters Laboratory
TM	Transition metal	ULAM	Ultra-low-angle microtomy
TMA	Trimethylamine; thermal mechanical analyzer	ULSD	Ultra-low sulfur diesel
TMAA	Trimethylamine alane adduct	um, µm	Micrometer(s)
TMAH	Tetramethylammonium hydroxide	UM	University of Michigan
TMB	Trimethylborate	UMC	Unsaturated metal centers; ultramicroporous carbon
TMEDA	Tetramethylethane-1,2-diamine	UN	United Nations
TMOS	Tetramethoxy silane	UNC	University of North Carolina
TMPP	Tetramethoxyphenyl porphyrins	UNLV	University of Nevada, Las Vegas
TMPS	Trimethoxyl phenyl silane	UNLVRF	UNLV Research Foundation
TOS	Time on stream	UNM	University of New Mexico
TPA	Tripropylamine; temperature-programmed adsorption	UNR	University of Nevada, Reno
TPAH	Tetra-n-propylammonium hydroxide	UPD	Underpotentially deposited
TPB	Triple phase boundary	UPE	Ultra-high molecular weight polyethylene
TPD	Tonne(s) per day; thermally programmed desorption; temperature-programmed desorption	UPS	Ultraviolet photoelectron spectroscopy
TPM	Technical performance measure	URFC	Unitized regenerative fuel cell
TPPS	5,10,15,20-tetrakis(4-sulfonatophenyl) porphyrin	U.S.	United States
TPO	Temperature-programmed oxidation	USA	United States of America
TPP	Tetraphenyl porphyrin	USB	Universal serial bus
TPR	Temperature-programmed reduction	USBPIC	Universal serial bus peripheral interface controller
TPRD	Thermally-activated pressure relief device	USC	University of South Carolina; University of Southern California
Trityl	Chemical blocking group used to protect amines	USCAR	United States Council for Automotive Research, U.S. Cooperative Automotive Research
tr. oz.	Troy ounce	USFCC	United States Fuel Cell Council
TV	Test vehicle	USM	University of Southern Mississippi
UC	University of California	USPP	Ultrasoft pseudopotentials
UCB	University of California, Berkeley	USTAG	U.S. Technical Advisory Group
		UTC, UTC FC	United Technologies Corporation Fuel Cells
		UTCP	UTC Power
		UTRC	United Technologies Research Center
		UV	Ultraviolet
		UV-vis	Ultraviolet-visual

V	Vanadium; volt	W/L, W/l	Watt(s) per liter
VAC	Volts alternating current	W/m-K, W/m.K, W/mK	
VANTA	Vertically aligned nanotube arrays		Watt(s) per meter-Kelvin (unit of thermal conductivity)
VASP	Vienna ab initio simulation package		
VaTech	Virginia Polytechnic Institute and State University	WMO	World Meteorological Organization
VBM	Valence band minimum	WO ₃	Tungsten trioxide
VC	Vulcan carbon	WOL	Wedge-opening load
VDC	Volts direct current	W-P	Water-propanol-isopropanol
VDF	Vinylidene fluoride	Wppm	Weight part(s) per million
VDOS	Vibrational density of states	WRI	Western Research Institute
vdW	van der Waals	wt	Weight
vdW-DF	van der Waals density function	Wt	Watt(s) thermal
V-I	Voltage – current	wt%, wt. %	Weight percent (percent by weight)
VIR	Voltage - current - resistance	WTP	Well-to-pump
VIS	Visible light at 400-700 nm	WTT	Well-to-tank
VL	Vacuum level	WTW	Well-to-wheels
VLS	Vapor-liquid-solid	w/v	Weight by volume
V _{mp}	Micropore volume	XANES	X-ray absorption near-edge spectroscopy
VMT	Vehicle miles travelled	XAS	X-ray absorption spectroscopy
VNT	Variable nozzle turbine	XC72	High-surface-area carbon support made by Cabot
VOC	Volatile organic compound; voltage open circuit	XES	X-ray emission spectroscopy
vol	Volume	XPS	X-ray photoelectron spectroscopy; X-ray photon spectroscopy; X-ray photoemission spectroscopy; X-ray photoluminescence spectroscopy
vol%	Volume percent	XRD	X-ray diffraction
V _{pore}	Total pore volume	XRF	X-ray fluorescence
VT	Virginia Tech	Y	Yttrium
W	Tungsten; Watt(s)	yr, YR	Year
WAXD	Wide-angle X-ray diffraction	YSZ	Yttria-stabilized zirconia
WAXS	Wide angle X-ray scattering	Z	Atomic number
WBS	Work breakdown schedule	ZIF	Zeolitic imidazolate framework
WC	Tungsten carbon, tungsten carbide	ZMOF	Zeolite(-type) metal-organic framework
W/cm ²	Watt(s) per square centimeter	Zn	Zinc
W _e	Watt(s) electric	ZnO	Zinc oxide
WGS	Water-gas shift	ZPE	Zero point energy
WGSMR	Water-gas shift membrane reactor	zpp	Zirconium phenyl phosphonate
WGSR	Water-gas shift reactor	Zr	Zirconium
Wh	Watt-hour(s)	ZrO ₂	Zirconium dioxide
W-h/kg	Watt-hour(s) per kilogram	ZrSPP	Zirconium phosphate sulfophenylphosphonate
W-h/L, Wh/L	Watt-hour(s) per liter	ZVI	Zerovalent iron
WHSV	Weight hourly space velocity		
Wind2H2	Wind to hydrogen demonstration project		
W/kg	Watt(s) per kilogram		

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